

# PATENT COOPERATION TREATY

**PCT**

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
US Department of Commerce  
United States Patent and Trademark  
Office, PCT  
2011 South Clark Place Room  
CP2/5C24  
Arlington, VA 22202  
ETATS-UNIS D'AMERIQUE  
in its capacity as elected Office

Date of mailing (day/month/year) 13 March 2001 (13.03.01)	
International application No. PCT/US00/19319	Applicant's or agent's file reference 60028
International filing date (day/month/year) 17 July 2000 (17.07.00)	Priority date (day/month/year) 16 July 1999 (16.07.99)
Applicant ALLGEUER, Thomas, T. et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
25 January 2001 (25.01.01)

☐ in a notice effecting later election filed with the International Bureau on:  
\_\_\_\_\_

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer <p style="text-align: center;">C. Cupello</p>
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>60028</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/US 00/19319</b>	International filing date (day/month/year) <b>17/07/2000</b>	(Earliest) Priority Date (day/month/year) <b>16/07/1999</b>
Applicant <b>THE DOW CHEMICAL COMPANY et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 05 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☒ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/19319

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B29C59/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 518 865 A (HOESSEL PETER ET AL) 21 May 1996 (1996-05-21) column 3, line 7 - line 11; example 1	1
X	EP 0 275 653 A (ICI PLC) 27 July 1988 (1988-07-27) column 3, line 9 - line 14 column 3, line 48 - line 52	1
X	GB 1 158 471 A (IMPERIAL CHEMICAL INDUSTRIES) 16 July 1969 (1969-07-16) example 1	1
X	DE 195 24 076 C (HCD HYGIENIC COMPOSITES DEV GM) 24 October 1996 (1996-10-24) cited in the application column 3, line 24 - line 27	1
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

20 October 2000

Date of mailing of the international search report

03. 11. 00

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Attalla, G

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/19319

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 208 773 A (ICI LTD) 28 June 1974 (1974-06-28) page 13, line 11 - line 16; figures ---	1
X	US 3 895 153 A (JOHNSTON MANLEY R ET AL) 15 July 1975 (1975-07-15) examples ---	1
P, X	DE 198 12 097 C (WAGNER) 2 September 1999 (1999-09-02) example 2 -----	1

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 00/19319

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 2-23  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 2-23

In view of the large number and also the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and concise), namely claim 1.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19319

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5518865 A	21-05-1996	DE 4141352 A AT 163096 T DE 59209181 D EP 0547419 A ES 2111601 T JP 5273758 A	17-06-1993 15-02-1998 12-03-1998 23-06-1993 16-03-1998 22-10-1993
EP 0275653 A	27-07-1988	AT 64845 T AU 605528 B AU 8257387 A CA 1298938 A DE 3771199 D DK 2188 A FI 875701 A JP 63181755 A NO 875260 A,B,	15-07-1991 17-01-1991 14-07-1988 21-04-1992 08-08-1991 08-07-1988 08-07-1988 26-07-1988 08-07-1988
GB 1158471 A	16-07-1969	NONE	
DE 19524076 C	24-10-1996	AT 196442 T AU 6418496 A WO 9702128 A EP 0836549 A JP 11508501 T	15-10-2000 05-02-1997 23-01-1997 22-04-1998 27-07-1999
FR 2208773 A	28-06-1974	GB 1451311 A AR 201674 A AT 364067 B AT 816977 A AT 344656 B AT 1014273 A AU 6284873 A BE 807879 A CA 1043068 A CA 1045322 A CA 1045323 A CH 566203 A DE 2359565 A DE 2365824 A DK 12888 A,B, DK 155190 B ES 421129 A IN 140101 A JP 49087762 A NL 7316259 A SE 393765 B SE 417291 B SE 7608985 A US 4451419 A US 4436687 A US 4436503 A ZA 7308898 A	29-09-1976 08-04-1975 25-09-1981 15-02-1981 10-08-1978 15-12-1977 29-05-1975 27-05-1974 28-11-1978 02-01-1979 02-01-1979 15-09-1975 27-06-1974 12-08-1976 12-01-1988 27-02-1989 16-04-1976 11-09-1976 22-08-1974 06-06-1974 23-05-1977 09-03-1981 11-08-1976 29-05-1984 13-03-1984 13-03-1984 25-06-1975
US 3895153 A	15-07-1975	AU 467758 B AU 7402274 A DE 2447989 A GB 1481876 A JP 869353 C	11-12-1975 11-12-1975 24-04-1975 03-08-1977 13-07-1977

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19319

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3895153 A		JP 50065536 A JP 51044010 B	03-06-1975 26-11-1976
DE 19812097 C	02-09-1999	AU 3413899 A WO 9947339 A	11-10-1999 23-09-1999



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NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

(PCT Rule 44.1)

From the INTERNATIONAL SEARCHING AUTHORITY

To:  
INTELLECTUAL PROPERTY  
Attn. PRIETO, Joe R.  
P.O. BOX 1967  
MIDLAND, MICHIGAN 48671-1967  
UNITED STATES OF AMERICA

Date of mailing  
(day/month/year)

03. 11. 00

Applicant's or agent's file reference

60028

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/US 00/19319

International filing date

(day/month/year)

17/07/2000

Applicant

THE DOW CHEMICAL COMPANY et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

John Berry

RECD 29 AUG 2001

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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

13

Applicant's or agent's file reference <b>60028</b>		<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. <b>PCT/US00/19319</b>	International filing date (day/month/year) <b>17/07/2000</b>	Priority date (day/month/year) <b>16/07/1999</b>	
International Patent Classification (IPC) or national classification and IPC <b>B29C59/02</b>			
Applicant <b>ADVANCED DESIGN CONCEPT GMBH et al.</b>			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 8 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of <u>2</u> sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the report</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input checked="" type="checkbox"/> Certain defects in the international application</p> <p>VIII <input checked="" type="checkbox"/> Certain observations on the international application</p>			
Date of submission of the demand  <b>25/01/2001</b>		Date of completion of this report  <b>27.08.2001</b>	
Name and mailing address of the international preliminary examining authority:   <b>European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465</b>		Authorized officer  <b>Deubler, U</b>  Telephone No. +49 89 2399 2923	



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/19319

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*):

**Description, pages:**

1-15,17-61	as originally filed	
16	as received on	18/12/2000

**Claims, No.:**

5-23	as originally filed		
1-4	as received on	10/08/2001	with letter of 08/08/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/19319

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 2 - 23.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☒ no international search report has been established for the said claims Nos. 2 - 23.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1
	No: Claims

Inventive step (IS)	Yes: Claims 1
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**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US00/19319

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	No:	Claims
Industrial applicability (IA)	Yes:	Claims 1
	No:	Claims

2. Citations and explanations  
**see separate sheet**

**VII. Certain defects in the international application**

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/US00/19319

**Re Item III**

**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

No search report has been prepared for claims 2 to 23 (see INTERNATIONAL SEARCH REPORT of 03.11.00).

Therefore no substantive novelty, inventive step and industrial applicability examination is possible with regard to claims 2 to 23.

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

The following documents (D) are referred to in this report :

- D1: US-A-5 518 865 (HOESSEL PETER ET AL) 21 May 1996 (1996-05-21)
- D2: EP-A-0 275 653 (ICI PLC) 27 July 1988 (1988-07-27)
- D3: GB-A-1 158 471 (IMPERIAL CHEMICAL INDUSTRIES) 16 July 1969 (1969-07-16)
- D4: DE 195 24 076 C (HCD HYGIENIC COMPOSITES DEV GM) 24 October 1996 (1996-10-24) cited in the application
- D5: FR-A-2 208 773 (ICI LTD) 28 June 1974 (1974-06-28)
- D6: US-A-3 895 153 (JOHNSTON MANLEY R ET AL) 15 July 1975 (1975-07-15)
- D7: DE 198 12 097 C (WAGNER) 2 September 1999 (1999-09-02)

- 1.) The invention relates to a mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer comprises substantially solid fibril-like fringes consisting of a thermoplastic polymeric material forming said layer.

A film of this type is known from e.g. document D3 or D4.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/US00/19319

The object of the invention is to provide plastic articles and items with a pleasant haptic appearance, such as textile-like touch and good optics.

This object is achieved according to the invention by the fringes having a minimum height of at least about 40 micron or more and said thermoplastic material being selected from the group consisting of

- a biodegradable polymer, preferably poly-lactide and
- a thermoplastic interpolymer comprising
  - i) polymer units derived from at least one of ethylene and/or an alpha-olefin monomer and
  - ii) polymer units derived from one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, or a combination of at least one aromatic vinyl or vinylidene monomer and
  - iii) optionally polymer units derived from one or more ethylenically unsaturated polymerizable monomers others than those derived from i) and ii).

None of the documents cited in the INTERNATIONAL SEARCH REPORT discloses or renders obvious the combination of these features in their entirety.

Therefore independent claim 1 meets the requirements of Articles 33 (2) and (3) PCT.

**Re Item VII**

**Certain defects in the international application**

- 1.) The description should have been brought into conformity with the new claim 1; care should have been taken during revision, especially of the introductory portion including any statements of problem or advantage, not to add subject-matter which extends beyond the content of the application as originally filed.

- 3.) The documents D1 to D7 have not been identified in the description nor has the relevant background art disclosed therein been discussed. The requirements of Rule 5.1(a)(ii) PCT are, thus, not fulfilled.
- 4.) It should also have been indicated in the description, which document represents the closest prior art.
- 5.) The object of the invention (single inventive concept) should have clearly been stated in the description (e.g. "It is the object of the invention to improve ... etc.") and this single object should completely be achieved by the invention as defined in the independent claim(s).

### **Re Item VIII**

#### **Certain observations on the international application**

- 1.) Although claims 1 to 23 have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought and/or in respect of the terminology used for the features of that subject-matter. The aforementioned claims therefore **lack conciseness**. Moreover, **lack of clarity** of the claims as a whole arises, since the plurality of independent claims makes it difficult, if not impossible, to determine the matter for which protection is sought, and places an undue burden on others seeking to establish the extent of the protection.  
Hence, claims 1 to 23 do not meet the requirements of Article 6 PCT.  
In order to overcome this objection, it would have been appropriate to file an amended set of claims defining the relevant subject-matter in terms of a **single independent claim in each category** followed by dependent claims covering features which are merely optional (Rule 6.4 PCT).
- 2.) In claim 1 the Applicant has used the term "characterized" twice, which renders



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/US00/19319

unclear what the actual pre-characterizing part (preamble) and the actual characterizing part of claim 1 is (Article 6 PCT).

To meet the requirements of Article 6 PCT and Rule 6.3(b) PCT the term "characterized" should have been used only once in claim 1.

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number  
WO 01/05573 A1

(51) International Patent Classification: B29C 59/02

Antonio [US/US]; 1506 Foxwood, Midland, MI 48642 (US).

(21) International Application Number: PCT/US00/19319

(74) Agent: PRIETO, Joe, R., Intellectual Property Section, P.O. Box 1967, Midland, MI 48641-1967 (US).

(22) International Filing Date: 17 July 2000 (17.07.2000)

(25) Filing Language: English

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.

(26) Publication Language: English

(30) Priority Data:  
60/144,306 16 July 1999 (16.07.1999) US  
60/153,793 14 September 1999 (14.09.1999) US

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(54) Title: THERMOPLASTIC ARTICLES COMPRISING A FRINGED SURFACE STRUCTURE

(57) Abstract: Disclosed are mono-layer or multi-layer films, sheets, or coatings wherein at least one layer comprises a surface microstructure characterized by substantially solid fibril-like fringes, a process for making these items and uses thereof. Further disclosed are articles of manufacture comprising such film, sheet, or coating.

## THERMOPLASTIC ARTICLES COMPRISING A FRINGED SURFACE STRUCTURE

FIELD OF THE INVENTION

5 This invention relates to an improved mono-layer or multi-layer film, sheet, or coating which comprises at least one layer which has or comprises a fringed surface microstructure. The invention also provides uses of such improved film, sheet or coating, as well as articles of manufacture made therefrom. Furthermore, the invention provides a new process to make a film, sheet or coating with a fringed surface microstructure.

10 BACKGROUND OF THE INVENTION

Plastic articles and items with a pleasant haptic appearance, such as a textile-like touch, and good optics are desirable for numerous applications, including hygienic products or garments. To improve aesthetics, for example of a plastic film, various techniques of surface modification have been employed, including, for example, extrusion under  
15 conditions favoring melt fracture, and embossing. Known surface modification processes to make solid surface features, particularly filament-like structures, include use of a calender roll or belt having holes in the surface, peeling films with a melted layer from an adherent surface forming fibrils upon removal and electrostatic flocking.

According to U.S. Patent No. 5,814,413 surface-texturing of a polymer film is  
20 accomplished by taking advantage of the usually undesired phenomenon of melt fracture. The patent discloses extruded films which due to melt fracture show a rough surface texture.

International Patent Application WO 99/16608 discloses a method for making an embossed oriented film. Said method discloses the steps of softening at least one of the  
25 two major surfaces of an oriented film, embossing the softened surface(s), and cooling the resulting embossed oriented thermoplastic film. In order to maintain orientation the combined steps of softening, embossing and cooling should occur within a second.

International Patent Application WO 97/02128 provides a process for producing a surface-structured, sheet-like semi-finished product made from thermoplastic polymers. The  
30 resulting product is reported to have a velour-like or velvety surface with numerous solid fibrous projections which can be longer than 3 millimeters. According to the disclosed process, the thermoplastic material is extruded in the molten state onto a moving belt or roller surface which is covered with cavities or borings having a depth of between 2 and 4 millimeters. The roller surface is exposed to a vacuum from the outside thus removing the

air from the cavities and enabling these to be filled with the thermoplastic material. After solidification of the thermoplastic material, the semi-finished product covered with fiber-like projections is peeled off the surface.

International Patent Application WO 99/47339 describes a method for producing a surface-structured, film-like semi-finished product from a thermoplastic comprising forming a pile consisting of solid protuberances and elongating the protuberances by combing, brushing, knife-coating and/or shear pinching.

International Patent Application WO 99/06623 provides a unitary polymer substrate having a plurality of solid microfibers which may have a variety of forms, such as frayed-end microfibers, tapered microfibers, microfibers having an expanded cross-sectional shape and microfibers having a high aspect ratio. The microfibers are reported to increase the surface area and to impart a cloth-like feel.

International Patent Application WO 00/16965 relates to a method for producing a surface-structured, film-like semifinished product made of a thermoplastic which is applied onto a surface covered with fine cavities. The solidified plastic is removed from the surface as a structured film. The disclosed structure is a pile comprised of solid projections and naps which may be stretched, e.g. by brushing.

U.S. Patent No. 5,792,411 suggests replicated articles with surface structures of various geometric configuration.

There still is the need for plastic articles with excellent aesthetics, as reflected in a textile-like haptic appearance and low gloss, showing further improved properties. Such properties include for example, , selected variability of the surface appearance, anti-slip behavior, controlled storage, release or carrier properties, controlled thermal performance, such as increased heat resistance, controlled barrier performance, and biodegradability, as well as any combination thereof.

It is an object of the present invention to meet these needs. It is an object of the present invention to provide improved surface-structured plastic films, sheets or coatings with substantially solid fiber-like structures which are specifically designed to meet a desired performance attribute, or a combination of performance attributes, and which can be produced in a cost effective way. It is an object of the present invention to provide a surface-structured plastic article with a printed or imprinted surface. The present invention also addresses the problem of providing a surface-structured plastic article having a

- frictional behavior indicating anti-slip properties. It is another object of the present invention to provide a surface-structured plastic article having increased heat resistance. It is yet another object of the present invention to provide a plastic article having enhanced storage, capturing or storing properties. It is yet another object of the present invention to provide a plastic article showing good water repellency.

It is a particular object of the present invention to provide a plastic article, which displays any desired combination of the above-mentioned properties, and may afford additional advantageous performance attributes depending on the intended end-use application or applications.

- The objects of the present invention are achieved by providing a film, sheet, or coating, which is characterized by a distinct morphology. Such morphology is reflected in the presence of at least one layer having a fringed surface microstructure and, optionally, of further layers affording certain additional functions, for example, heat sealability, bulk or mechanical properties. The morphology and composition of the film, sheet or coating of the invention can be tailored to satisfy the particular requirements of the production process and the intended end-use application(s).

#### SUMMARY OF THE INVENTION

- The present invention pertains to a mono-layer or multi-layer film, sheet, or coating. The film, sheet or coating of the invention comprises at least one layer which is a thermoplastic polymeric material and which is characterized by a fringed surface microstructure. The fringes are substantially solid fiber-like surface aberrations. The density of the fringes is at least 1000 per square centimeter, or higher. The layer is covered by the fringed microstructure on its entire surface, in one part, or in parts of its surface. The fringed surface microstructure may be discernible with the naked eye or on appropriate magnification. This includes a cured, irradiated or cross-linked film, sheet or coating, as well as a film, sheet, or coating comprising a cured, radiated or cross-linked material. The fringed layer may carry fringes on one or both (surface) sides, whether exposed (to the outside) or present as an interlayer surface.

In another aspect, the invention relates to a mono-layer or multi-layer foamed film, sheet or coating comprising a fringed microstructure.

Another aspect of the invention relates to a composite comprising a mono-layer or multi-layer film, sheet, or coating based on a thermoplastic polymeric material wherein at least one layer has a fringed surface microstructure.

Another aspect of the invention relates to an article of manufacture comprising or  
5 made from a mono-layer or multi-layer film, sheet, or coating based on a thermoplastic polymeric material wherein at least one layer has a fringed surface microstructure.

Another aspect of the invention relates to a process for making the film, sheet, or coating based on a thermoplastic polymeric material wherein at least one layer has a fringed surface microstructure, said process comprising:

- 10       - providing a foamed precursor film, sheet, or coating with a surface characterized by a pattern of peaks and valleys, and  
      - treating said precursor such as to create a surface having a fringed microstructure. Preferably, the treatment is mechanical in nature.

Yet another aspect of the invention relates to the use of a mono- or multi-layer film,  
15 sheet, or coating which is based on a thermoplastic polymeric material and wherein at least one layer has or comprises the fringed surface microstructure in applications or articles which benefit from specifically designed advantageous performance attributes provided by the fringed surface microstructure, the thermoplastic polymeric material, or both.

20       DETAILED DESCRIPTION OF THE INVENTION

Basic Definitions

The term "film" as used herein refers to a thin article and includes strips, tapes, and ribbons. The article has a flat form and a thickness of about 10 mils (250 microns (\*m) or micrometer), or less. Thickness data for a film having a fringed surface microstructure  
25 generally exclude the fringe height.

The term "sheet" as used herein refers to a flat article having a thickness of greater than about 10 mils (250 microns).

The term "coating" as used herein refers to a material applied over or on top of a substrate material. The substrate material (or its surface) can be of any shape, form or  
30 contour. Also, the substrate surface can be made from a thermoplastic or a non-thermoplastic material such as, for example, but not limited to, polyethylene, polypropylene,

paper, glass, ceramic, cardboard, foil, wood or wood-based materials, such as particleboard or fiberboard, and metal, such as copper.

- The term "multi-layer film, sheet, or coating" (including each individually e.g. "multi-layer film") as used herein indicates a film, sheet, or coating consisting of two, three, four, five, six, seven or more layers.

The term "foamed film, sheet, or coating" (including each individually e.g. "foamed film") as used herein refers to a mono-layer or multi-layer structure wherein at least one layer of the structure is foamed and has a density less than the non-foamed layer or polymer.

- The term "composite" as used herein refers to a multi-layer or multi-component article or material comprising at least one film, sheet, or coating layer having a fringed surface structure, (including, for example, but not limited to, a fabric or a laminated structure which may comprise, for example foil or paper).

- The term "polymeric material" as used herein refers to a polymeric compound obtainable by polymerizing one or more monomers. The generic term "polymeric compound" or "polymer" is intended to include a homopolymer, usually employed to refer to polymers prepared from only one monomer, and an interpolymar as defined hereinafter.

The term "comprising" as used herein means "including".

- The term "interpolymer" as used herein refers to polymers prepared by the polymerization of at least two monomers. The generic term interpolymar thus embraces the terms copolymer, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different monomers, such as terpolymers.

- Unless specified otherwise, the term "alpha-olefin" (" $\alpha$ -olefin") as used herein refers to an aliphatic or cyclo-aliphatic alpha-olefin having at least 3, preferably 3 to 20 carbon atoms.

- Unless indicated to the contrary, all parts, percentages and ratios are by weight. The expression "up to" when used to specify a numerical range includes any value less than or equal to the numerical value which follows this expression. The expressions "cc" or "ccm" stand for "cubic centimeters".

### Thermoplastic Materials

The film, sheet, or coating of the invention is based on or made from one or more thermoplastic polymeric materials, including, for example, latex. Preferred thermoplastic polymeric materials are semicrystalline polymers, amorphous polymers, or blends thereof.

5 Advantageously, suitable thermoplastic polymers may be selected from the group consisting of polyolefins, poly(lactide), alkenyl aromatic polymers, thermoplastic polyurethanes, polycarbonates, polyamides, polyethers, thermoplastic phenoxy resins, polyvinyl chloride polymers, polyvinylidene chloride polymers and polyesters, including certain elastomers and block polymers. Semicrystalline thermoplastic materials and blends thereof are preferred.

10 Suitable polyolefins include, for example, ethylene-based polymers, including ethylene homopolymer and interpolymers, aliphatic  $\alpha$ -olefin homopolymers, such as polypropylene, polybutene and polyisoprene, and their interpolymers.

Ethylene homopolymers, for example low density polyethylene (LDPE) and high density polyethylene (HDPE), and ethylene interpolymers are known classes of  
15 thermoplastic polymers, each having many members. They are prepared by homopolymerizing ethylene or interpolymers (for example, copolymerizing) ethylene with one or more vinyl- or diene-based comonomers, for example,  $\alpha$ -olefins of 3 to about 20 carbon atoms, vinyl esters, vinyl acids, styrene-based monomers, monomers containing two or more sites of ethylenic unsaturation, etc., using known copolymerization reactions and  
20 conditions.

Ethylene (based) polymers suitable for use in the present invention include both homogeneously branched (homogeneous) polymers and heterogeneously branched (heterogeneous) polymers.

"Homogeneous" polymers encompass ethylene-based interpolymers in which any  
25 comonomer is randomly distributed within a given interpolymers molecule and substantially all of the interpolymers molecules have the same ethylene/comonomer ratio within that interpolymers. Homogeneous ethylene polymers generally are characterized as having an essentially single melting (point) peak between -30°C and 150°C, as determined by differential scanning calorimetry (DSC). The single melting peak may be relatively broad,  
30 such as is the case when an ethylene polymer having a crystallinity of less than about 36 percent is employed. The single melting peak may be sharp, such as is the case when an ethylene polymer having a crystallinity of at least about 36 percent is employed.



- Typically, homogeneous ethylene polymers will also have a relatively narrow molecular weight distribution (MWD) as compared to corresponding heterogeneous ethylene polymers. Preferably, the molecular weight distribution defined as the ratio of weight average molecular weight to number average molecular weight ( $M_w/M_n$ ), is less than about 3.5 (when the density of the interpolymer is less than about 0.960 g/cc), more preferably less than about 3.0.

- In addition or in the alternative, the homogeneity of the ethylene-based polymers is reflected in a narrow composition distribution, which can be expressed using parameters such as SCBDI (Short Chain Branch Distribution Index) or (CDBI Composition Distribution Branch Index). The SCBDI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), in U.S. Patent 4,798,081 (Hazlitt et al.), or in U.S. Patent 5,089,321 (Chum et al.), the disclosures of all of which are incorporated herein by reference. CDBI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The SCBDI or CDBI for the homogeneous linear and substantially linear ethylene/alpha-olefin polymers used in the present invention is typically greater than about 50 percent.

- The homogeneous ethylene polymers that can be used in the present invention fall into two broad categories, the linear homogeneous ethylene polymers and the substantially linear homogeneous ethylene polymers. Both are known.

- Homogeneous linear ethylene polymers have long been commercially available. As exemplified in U.S. Patent No. 3,645,992 to Elston, homogeneous linear ethylene polymers can be prepared in conventional polymerization processes using Ziegler-type catalysts such as, for example, zirconium and vanadium catalyst systems. U.S. Patent No. 4,937,299 to Ewen et al. and U.S. Patent No. 5,218,071 to Tsutsui et al. disclose the use of metallocene catalysts, such as catalyst systems based on hafnium, for the preparation of homogeneous linear ethylene polymers. Commercially available examples of homogeneous linear ethylene polymers include, for example, those sold by Mitsui Petrochemical Industries as TAFMER™ resins and by Exxon Chemical Company as EXACT™ and EXCEED™ resins.

The substantially linear ethylene polymers (SLEPs) are homogeneous polymers having long chain branching.

The term "substantially linear ethylene polymer" as used herein means that the bulk ethylene polymer is substituted, on average, with about 0.01 long chain branches/1000 total carbons to about 3 long chain branches/1000 total carbons (wherein "total carbons" includes both backbone and branch carbon atoms). Preferred polymers are substituted with about 0.01 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons, more preferably from about 0.05 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons, and especially from about 0.3 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons.

As used herein, the term "backbone" refers to a discrete molecule, and the term "polymer" or "bulk polymer" refers, in the conventional sense, to the polymer as formed in a reactor. For the polymer to be a "substantially linear ethylene polymer", the polymer must have at least enough molecules with long chain branching such that the average long chain branching in the bulk polymer is at least an average of from about 0.01/1000 total carbons to about 3 long chain branches/1000 total carbons.

The term "bulk polymer" as used herein means the polymer which results from the polymerization process as a mixture of polymer molecules and, for substantially linear ethylene polymers, includes molecules having an absence of long chain branching as well as molecules having long chain branching. Thus a "bulk polymer" includes all molecules formed during polymerization. It is understood that, for the substantially linear polymers, not all molecules have long chain branching, but a sufficient amount do such that the average long chain branching content of the bulk polymer positively affects the melt rheology (i.e., the melt fracture properties) as described herein below and elsewhere in the literature.

Long chain branching (LCB) is defined herein as a chain length of at least one (1) carbon (atom) less than the number of carbons in the comonomer, whereas short chain branching (SCB) is defined herein as a chain length of the same number of carbons in the residue of the comonomer after it is incorporated into the polymer molecule backbone. For example, a substantially linear ethylene/1-octene polymer has backbones with long chain branches of at least seven (7) carbons in length, but it also has short chain branches of only six (6) carbons in length.

Long chain branching can be distinguished from short chain branching by using  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy and to a limited extent, e.g. for ethylene homopolymers; it can be quantified using the method of Randall, (Rev. Macromol.Chem. Phys., **C29** (2&3), p. 285-297), the disclosure of which is incorporated herein by reference.

However as a practical matter, current  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of about six (6) carbon atoms and as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch. The long chain branch can be as long as about the same length as the length of the polymer backbone.

Although conventional  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of six carbon atoms, there are other known techniques useful for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. For example, US Patent No. 4,500,648, incorporated herein by reference, teaches that long chain branching frequency (LCB) can be represented by the equation  $\text{LCB} = b/M_w$  wherein  $b$  is the weight average number of long chain branches per molecule and  $M_w$  is the weight average molecular weight. The molecular weight averages and the long chain branching characteristics are determined by gel permeation chromatography and intrinsic viscosity methods, respectively.

Two other useful methods for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, e.g., Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949) and Rudin, A., Modern Methods of Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112, the disclosures of both of which are incorporated by reference.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the October 4, 1994 conference of the Federation of Analytical Chemistry and Spectroscopy Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is indeed a useful technique for quantifying the presence of long chain branches in substantially linear ethylene polymers. In particular, deGroot and Chum found that the level of long chain branches in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer equation correlated well with the level of long chain branches measured using  $^{13}\text{C}$ -NMR.

Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the polyethylene samples in solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short chain branches, deGroot and Chum showed that GPC-DV may be used to quantify the level of long chain branches in substantially linear ethylene/octene copolymers.

DeGroot and Chum also showed that a plot of  $\log(I_2, \text{melt index})$  as a function of  $\log(\text{GPC Weight Average Molecular Weight})$  as determined by GPC-DV illustrates that the long chain branching aspects (but not the extent of long branching) of substantially linear ethylene polymers are comparable to that of high pressure, highly branched low density polyethylene (LDPE) and are clearly distinct from ethylene polymers produced using Ziegler-type catalysts such as titanium complexes and ordinary homogeneous catalysts such as hafnium and vanadium complexes.

For substantially linear ethylene polymers, the empirical effect of the presence of long chain branching is manifested as enhanced rheological properties which are quantified and expressed in terms of gas extrusion rheometry (GER) results and/or melt flow,  $I_{10}/I_2$ , increases.

The substantially linear ethylene polymers suitable for the purpose of the present invention are a unique class of compounds that are further defined in US Patent No. 5,272,236, US Patent No. 5,278,272, and US Patent No. 5,665,800, each of which is incorporated herein by reference. SLEPs are available from The Dow Chemical Company as polymers made by the INSITE™ Process and Catalyst Technology, such as AFFINITY™ polyolefin plastomers (POPs), and from DuPont Dow Elastomers, L.L.C. as ENGAGE™ polyolefin elastomers (POEs).

Substantially linear ethylene polymers differ significantly from the class of polymers conventionally known as homogeneously branched linear ethylene polymers described above. As an important distinction, substantially linear ethylene polymers do not have a linear polymer backbone in the conventional sense of the term "linear" as is the case for homogeneously branched linear ethylene polymers. Substantially linear ethylene polymers also differ significantly from the class of polymers known conventionally as heterogeneously branched traditional Ziegler polymerized linear ethylene interpolymers (for example, ultra low density polyethylene, linear low density polyethylene (LLDPE) or high density

polyethylene (HDPE) made, for example, using the technique disclosed by Anderson et al. in US Patent No. 4,076,698, in that substantially linear ethylene interpolymers are homogeneously branched polymers; that is, substantially linear ethylene polymers have a SCBDI greater than or equal to 50 percent, preferably greater than or equal to 70 percent, more preferably greater than or equal to 90 percent. Substantially linear ethylene polymers also differ from the class of heterogeneously branched ethylene polymers in that substantially linear ethylene polymers are characterized as essentially lacking a measurable high density or crystalline polymer fraction as determined using a temperature rising elution fractionation technique.

10 The substantially linear ethylene polymer for use in the present invention can be characterized as having

- (a) melt flow ratio,  $I_{10}/I_2 \cdot 5.63$ ,
- (b) a molecular weight distribution,  $M_w/M_n$ , as determined by gel permeation chromatography and defined by the equation:

15 
$$(M_w/M_n) \leq (I_{10}/I_2) - 4.63,$$

(c) a gas extrusion rheology such that the critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a linear ethylene polymer, wherein the substantially linear ethylene polymer and the linear ethylene polymer  
20 comprise the same comonomer or comonomers, the linear ethylene polymer has an  $I_2$  and  $M_w/M_n$  within ten percent of the substantially linear ethylene polymer and wherein the respective critical shear rates of the substantially linear ethylene polymer and the linear ethylene polymer are measured at the same melt temperature using a gas extrusion rheometer,

25 (d) a single differential scanning calorimetry, DSC, melting peak between -30°C and 150°C, and

(e) a short chain branching distribution index greater than 50 percent.

Determination of the critical shear rate and critical shear stress in regards to melt fracture as well as other rheology properties such as "rheological processing index" (PI), is  
30 performed using a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, No. 11, p. 770 (1977) and in Rheometers for Molten Plastics by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97-99, the disclosures of both of which are

incorporated herein by reference.

- The processing index (PI) is measured at a temperature of 190°C, at nitrogen pressure of 2500 psig using a 0.0296 inch (752 micrometers) diameter (preferably a 0.0143 inch diameter die for high flow polymers, e.g. 50 - 100 I<sub>2</sub> melt index or greater), 20:1 L/D die having an entrance angle of 180°. The GER processing index is calculated in millipoise units from the following equation:

$$PI = 2.15 \times 10^6 \text{ dyne/cm}^2 / (1000 \times \text{shear rate}),$$

wherein:  $2.15 \times 10^6 \text{ dyne/cm}^2$  is the shear stress at 2500 psi, and the shear rate is the shear rate at the wall as represented by the following equation:

$$32 Q' / (60 \text{ sec/min})(0.745)(\text{Diameter} \times 2.54 \text{ cm/in})^3, \text{ wherein:}$$

$Q'$  is the extrusion rate (gms/min),

0.745 is the melt density of polyethylene (gm/cm<sup>3</sup>), and

Diameter is the orifice diameter of the capillary (inches).

- The PI is the apparent viscosity of a material measured at apparent shear stress of  $2.15 \times 10^6 \text{ dyne/cm}^2$ .

For substantially linear ethylene polymers, the PI is less than or equal to 70 percent of that of a conventional linear ethylene polymer having an I<sub>2</sub>, M<sub>w</sub>/M<sub>n</sub> and density each within ten percent of the substantially linear ethylene polymer.

- An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena over a range of nitrogen pressures from 5250 to 500 psig using the die or GER test apparatus previously described. According to Ramamurthy in Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

- Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40x magnification. The critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I<sub>2</sub> and M<sub>w</sub>/M<sub>n</sub>.

Preferably, the critical shear stress at onset of surface melt fracture for the substantially linear ethylene polymers of the invention is greater than about  $2.8 \times 10^6$  dyne/cm<sup>2</sup>.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and critical shear stress at onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. For the substantially linear ethylene polymers used in the invention, the critical shear stress at onset of gross melt fracture is preferably greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>.

For the processing index determination and for the GER melt fracture determination, substantially linear ethylene polymers are tested without inorganic fillers and do not have more than 20 ppm aluminum catalyst residue. Preferably, however, for the processing index and melt fracture tests, substantially linear ethylene polymers do contain antioxidants such as phenols, hindered phenols, phosphites or phosphonites, preferably a combination of a phenol or hindered phenol and a phosphite or a phosphonite.

The molecular weight distributions of ethylene polymers are determined by gel permeation chromatography (GPC) on a Waters 150 °C high temperature chromatographic unit equipped with a differential refractometer and three columns of mixed porosity. The columns are supplied by Polymer Laboratories and are commonly packed with pore sizes of  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6$  Å. The solvent is 1,2,4-trichlorobenzene, from which about 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is about 1.0 milliliters/minute, unit operating temperature is about 140°C and the injection size is about 100 microliters.

The molecular weight determination with respect to the polymer backbone is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, p. 621, 1968, the disclosure of which is incorporated herein by reference) to derive the following equation:

$$M_{\text{polyethylene}} = a \cdot (M_{\text{polystyrene}})^b$$

In this equation,  $a = 0.4316$  and  $b = 1.0$ . Weight average molecular weight,  $M_w$ , is calculated in the usual manner according to the following formula:

$$M_j = (\sum w_i (M_i)^j);$$

- wherein  $w_i$  is the weight fraction of the molecules with molecular weight  $M_i$ ,  
 5 eluting from the GPC column in fraction  $i$  and  $j = 1$  when calculating  $M_w$  and  $j = -1$  when calculating  $M_n$ .

- Substantially linear ethylene polymers are known to have excellent processability, despite having a relatively narrow molecular weight distribution (that is, the  $M_w/M_n$  ratio is typically less than about 3.5). Surprisingly, unlike homogeneously and heterogeneously  
 10 branched linear ethylene polymers, the melt flow ratio ( $I_{10}/I_2$ ) of substantially linear ethylene polymers can be varied essentially independently of the molecular weight distribution,  $M_w/M_n$ .

- Suitable constrained geometry catalysts for manufacturing substantially linear ethylene polymers include constrained geometry catalysts as disclosed in U.S. application  
 15 number 07/545,403, filed July 3, 1990; U.S. application number 07/758,654, filed September 12, 1991; U.S. Patent No. 5,132,380; U.S. Patent No. 5,064,802; U.S. Patent No. 5,470,993; U.S. Patent No. 5,453,410; U.S. Patent No. 5,374,696; U.S. Patent No. 5,532,394; U.S. Patent No. 5,494,874; and U.S. Patent No. 5,189,192, the teachings of all of which are incorporated herein by reference.

- Suitable catalyst complexes may also be prepared according to the teachings of WO  
 20 93/08199, and the patents issuing therefrom, all of which are incorporated herein by reference. Further, the monocyclopentadienyl transition metal olefin polymerization catalysts taught in U.S. Patent No. 5,026,798, which is incorporated herein by reference, are also believed to be suitable for use in preparing the polymers of the present invention,  
 25 so long as the polymerization conditions substantially conform to those described in US Patent No. 5,272,236; US Patent No. 5,278,272 and US Patent No. 5,665,800, especially with strict attention to the requirement of continuous polymerization. Such polymerization methods are also described in PCT/US 92/08812 (filed October 15, 1992).

- The foregoing catalysts may be further described as comprising a metal coordination  
 30 complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalize  $\beta$ -bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the



angle at the metal between the centroid of the delocalized, substituted pi-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar pi-bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted pi-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted pi-bonded moiety. The catalyst further comprises an activating cocatalyst.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. So called modified methyl aluminoxane (MMAO) is also suitable for use as a cocatalyst. One technique for preparing such modified aluminoxane is disclosed in US Patent No. 5,041,584, the disclosure of which is incorporated herein by reference. Aluminoxanes can also be made as disclosed in US Patent No. 5,218,071; US Patent No. 5,086,024; US Patent No. 5,041,585; US Patent No. 5,041,583; US Patent No. 5,015,749; US Patent No. 4,960,878; and US Patent No. 4,544,762, the disclosures of all of which are incorporated herein by reference.

Aluminoxanes, including modified methyl aluminoxanes, when used in the polymerization, are preferably used such that the catalyst residue remaining in the (finished) polymer is preferably in the range of from about 0 to about 20 ppm aluminum, especially from about 0 to about 10 ppm aluminum, and more preferably from about 0 to about 5 ppm aluminum. In order to measure the bulk polymer properties (e.g. PI or melt fracture), aqueous HCl is used to extract the aluminoxane from the polymer. Preferred cocatalysts, however, are inert, noncoordinating, boron compounds such as those described in EP-A-0520732, the disclosure of which is incorporated herein by reference.

Substantially linear ethylene are produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor (e.g., as disclosed in WO 93/07187, WO 93/07188, and WO 93/07189, the disclosure of each of which is incorporated herein by reference), but can also be produced using multiple reactors (e.g., using a multiple reactor configuration as described in US Patent No. 3,914,342, the disclosure of which is incorporated herein by reference) at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties. The multiple reactors can be operated in series or in parallel, with at least one constrained geometry catalyst employed in at least one of the reactors.

Substantially linear ethylene polymers can be prepared via the continuous solution, slurry, or gas phase polymerization in the presence of a constrained geometry catalyst; such as the method disclosed in EP-A-416,815, the disclosure of which is incorporated herein by reference. The polymerization can generally be performed in any reactor system known in the art including, but not limited to, a tank reactor(s), a sphere reactor(s), a recycling loop reactor(s) or combinations thereof and the like, any reactor or all reactors operated partially or completely adiabatically, nonadiabatically or a combination of both and the like. Preferably, a continuous loop-reactor solution polymerization process is used to manufacture the substantially linear ethylene polymer used in the present invention.

In general, the continuous polymerization required to manufacture substantially linear ethylene polymers may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired.

A support may be employed in the polymerization, but preferably the catalysts are used in a homogeneous (i.e., soluble) manner. It will, of course, be appreciated that the active catalyst system forms *in situ* if the catalyst and the cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

Preferably, the substantially linear ethylene polymers used in the present invention are interpolymers of ethylene with at least one C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -olefin and/or C<sub>4</sub>-C<sub>18</sub> diolefin, in accordance with the definitions and preferences given hereinbelow. Copolymers of ethylene and an  $\alpha$ -olefin of C<sub>3</sub>-C<sub>20</sub> carbon atoms are preferred.

Heterogeneous ethylene-based polymers encompass ethylene/ $\alpha$ -olefin interpolymers characterized as having a linear backbone and a DSC melting curve having a distinct melting point peak greater than 115°C attributable to a high density fraction. Such heterogeneous interpolymers will typically have a broader molecular weight distribution than homogeneous interpolymers, as reflected in a  $M_w/M_n$  ratio of greater than about 3.5 (when the density of the interpolymers is less than about 0.960 g/cc). Typically, heterogeneous ethylene interpolymers have a CDBI of about 50 % or less, indicating that such

interpolymers are a mixture of molecules having differing comonomer contents and differing amounts of short chain branching.

The heterogeneous ethylene polymers that can be used in the practice of this invention fall into two broad categories, those prepared with a free radical initiator at high temperature and high pressure, and those prepared with a coordination catalyst at high temperature and relatively low pressure. The former are generally known as low density polyethylenes (LDPE) and are characterized by branched chains of polymerized monomer units pendant from the polymer backbone. LDPE polymers generally have a density between about 0.910 and 0.935 g/cc. Ethylene polymers and copolymers prepared by the use of a coordination catalyst, such as a Ziegler or Phillips catalyst, are generally known as linear polymers because of the substantial absence of branch chains of polymerized monomer units pendant from the backbone. High density polyethylene (HDPE), generally having a density of about 0.941 to about 0.965 g/cc, is typically a homopolymer of ethylene, and it contains relatively few branch chains relative to the various linear copolymers of ethylene and an  $\alpha$ -olefin. HDPE is well known, commercially available in various grades, and may be used in this invention.

Linear copolymers of ethylene and at least one  $\alpha$ -olefin of 3 to 12 carbon atoms, preferably of 4 to 8 carbon atoms, are also well known and commercially available. As is well known in the art, the density of a linear ethylene/ $\alpha$ -olefin copolymer is a function of both the length of the  $\alpha$ -olefin and the amount of such monomer in the copolymer relative to the amount of ethylene, the greater the length of the  $\alpha$ -olefin and the greater the amount of  $\alpha$ -olefin present, the lower the density of the copolymer. Linear low density polyethylene (LLDPE) is typically a copolymer of ethylene and an  $\alpha$ -olefin of 3 to 12 carbon atoms, preferably 4 to 8 carbon atoms (for example, 1-butene, 1-octene, etc.), that has sufficient  $\alpha$ -olefin content to reduce the density of the copolymer to that of LDPE. When the copolymer contains even more  $\alpha$ -olefin, the density will drop below about 0.91 g/cc and these copolymers are known as ultra low density polyethylene (ULDPE) or very low density polyethylene (VLDPE). The densities of these linear polymers generally range from about 0.87 g/cc to about 0.91 g/cc.

Both the materials made by the free radical catalysts and by the coordination catalysts are well known in the art, as are their methods of preparation. For example, heterogeneous linear ethylene polymers are available from The Dow Chemical Company as DOWLEX™ LLDPE polymers and as ATTANET™ ULDPE resins. Heterogeneous linear

ethylene polymers can be prepared via the solution, slurry or gas phase polymerization of ethylene and one or more optional  $\alpha$ -olefin comonomers in the presence of a Ziegler Natta catalyst, by processes such as are disclosed in U.S. Patent No. 4,076,698 to Anderson et al., which is incorporated herein by reference.

- 5 As indicated above, the ethylene polymers suitable for the purpose of the present invention can be interpolymers of ethylene and at least one  $\alpha$ -olefin. Suitable  $\alpha$ -olefins for use as comonomers in a solution, gas phase or slurry polymerization process or combinations thereof include 1-propylene, 1-butene, 1-isobutylene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene and 1-octene, as well as other monomer types such as
- 10 tetrafluoroethylene, vinyl benzocyclobutane, 1,4-hexadiene, 1,7-octadiene, and cycloalkenes, for example cyclopentene, cyclohexene, cyclooctene, norbornene (NB), and ethylidene norbornene (ENB)). Preferably, the  $\alpha$ -olefin will be 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, NB or ENB, or mixtures thereof. More preferably, the  $\alpha$ -olefin will be 1-pentene, 1-hexene, 1-heptene, 1-octene, or mixtures
- 15 thereof. Most preferably, the  $\alpha$ -olefin will be 1-octene.

- Ethylene/ $\alpha$ -olefin/diene terpolymers may also be used as elastomeric polymers in this invention. Suitable  $\alpha$ -olefins include the  $\alpha$ -olefins described above as suitable for making ethylene  $\alpha$ -olefin copolymers. The dienes suitable as monomers for the preparation of such terpolymers are typically non-conjugated dienes having from 6 to 15 carbon atoms.
- 20 Representative examples of suitable non-conjugated dienes that may be used to prepare the terpolymer include:

- a) Straight chain acyclic dienes such as 1,4-hexadiene, 1,5-heptadiene, and 1,6-octadiene;
  - b) branched chain acyclic dienes such as 5-methyl-1, 4-hexadiene, 3,7-dimethyl-1-6-octadiene, and 3,7-dimethyl-1,7-octadiene;
  - c) single ring alicyclic dienes such as 4-vinylcyclohexene, 1-allyl-4-isopropylidene cyclohexane, 3-allylcyclopentene, 4-allylcyclohexene, and 1-isopropenyl-4-butenylcyclohexane;
  - d) multi-ring alicyclic fused and bridged ring dienes such as dicyclopentadiene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene, 5-methylene-6-methyl-2-norbornene, 5-methylene-6, 6-dimethyl-2-norbornene, 5-propenyl-2-norbornene, 5-(3-cyclopentenyl)-2-
- 25
- 30

norbornene, 5-ethylidene-2-norbornene, 5-cyclohexylidene-2-norbornene, etc.

The preferred dienes are selected from the group consisting of 1,4-hexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 7-methyl-1, 6-octadiene, piperylene, 4-vinylcyclohexene, etc.

The preferred terpolymers for the practice of the invention are terpolymers of ethylene, propylene and a non-conjugated diene (EPDM). Such terpolymers are commercially available. Ethylene/ $\alpha$ -olefin/diene terpolymers are useful when it is desired to make elastomeric polymer blends vulcanizable with the well known sulfur compound vulcanization process.

Ethylene/unsaturated carboxylic acid, salt and ester interpolymers may also be used in this invention. These are interpolymers of ethylene with at least one comonomer selected from the group consisting of vinyl esters of a saturated carboxylic acid wherein the acid moiety has up to 4 carbon atoms, unsaturated mono- or dicarboxylic acids of 3 to 5 carbon atoms, a salt of the unsaturated acid, esters of the unsaturated acid derived from an alcohol having 1 to 8 carbon atoms, and mixtures thereof. Terpolymers of ethylene and these comonomers are also suitable. Ionomers, which are completely or partially neutralized copolymers of ethylene and the acids described above, are discussed in more detail in U.S. Patent 3,264,272, already incorporated herein by reference. In addition, terpolymers of ethylene/vinyl acetate/carbon monoxide or ethylene/methyl acrylate/carbon monoxide containing up to about 15 percent by weight of carbon monoxide can also be employed.

Suitable ethylene/unsaturated carboxylic acid, salt and ester interpolymers include ethylene/vinyl acetate (EVA) including, but not limited to, the stabilized EVA described in U.S. Patent 5,096,955, which is incorporated herein by reference; ethylene/acrylic acid (EAA) and its ionomers; ethylene/methacrylic acid and its ionomers; ethylene/methyl acrylate; ethylene/ethyl acrylate; ethylene/isobutyl acrylate; ethylene/normal butyl acrylate; ethylene/isobutyl acrylate/methacrylic acid and its ionomers; ethylene/normal butyl acrylate/methacrylic acid and its ionomers; ethylene/isobutyl acrylate/acrylic acid and its ionomers; ethylene/normal butyl acrylate/acrylic acid and its ionomers; ethylene/methyl methacrylate; ethylene/vinyl acetate/methacrylic acid and its ionomers; ethylene/vinyl acetate/acrylic acid and its ionomers; ethylene/vinyl acetate/carbon monoxide; ethylene/methacrylate/carbon monoxide; ethylene/normal butyl acrylate/carbon monoxide;

ethylene/isobutyl acrylate/carbon monoxide; ethylene/vinyl acetate/monoethyl maleate and ethylene/methyl acrylate/monoethyl maleate. Particularly suitable copolymers are EVA; EAA; ethylene/methyl acrylate; ethylene/isobutyl acrylate; and ethylene/methyl methacrylate copolymers and mixtures thereof. Certain properties, such as tensile elongation, are taught to be improved by certain combinations of these ethylene interpolymers described in U. S. Patent 4,379,190, which is incorporated herein by reference. The procedures for making these ethylene interpolymers are well known in the art and many are commercially available.

Propylene based polymers are also suitable to make a film, sheet, or coating according to this invention. Such propylene based polymers are, for example, homopolypropylene and propylene interpolymers, such as copolymers of propylene with ethylene and/or a  $C_4-C_{20}$  alpha-olefin, including impact copolymers and polypropylene random copolymers.

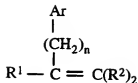
Further thermoplastic interpolymers suitable to practice the present invention are polyolefin interpolymers comprising

- i) polymer units derived from at least one of ethylene and/or an alpha-olefin monomer; and
- ii) polymer units derived from one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, or a combination of at least one aromatic vinyl or vinylidene monomer, and
- iii) optionally polymer units derived from one or more ethylenically unsaturated polymerizable monomer(s) other than those derived from i) and ii).

Suitable  $\alpha$ -olefins include, for example,  $\alpha$ -olefins containing from 3 to about 20, preferably from 3 to about 12, more preferably from 3 to about 8 carbon atoms. These  $\alpha$ -olefins do not contain an aromatic moiety. Particularly suitable are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1 or ethylene in combination with one or more of propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1.

Polymerizable ethylenically unsaturated monomer(s) include strained ring olefins such as norbornene and  $C_4-C_{10}$  alkyl or  $C_6-C_{10}$  aryl substituted norbornenes, with an exemplary interpolymers being ethylene/styrene/norbornene.

Suitable vinyl or vinylidene aromatic monomers include, for example, those represented by the following formula:



- wherein R<sup>1</sup> is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R<sup>2</sup> is
- 5 independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C<sub>1</sub>-C<sub>4</sub>-alkyl, and C<sub>1</sub>-C<sub>4</sub>-haloalkyl; and n has a value from zero to about 4, preferably from zero to 2, most preferably zero. Exemplary vinyl aromatic monomers
- 10 include styrene, vinyl toluene, α-methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and the like. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, α-methyl styrene, the lower alkyl-(C<sub>1</sub>-C<sub>4</sub>) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring
- 15 halogenated styrenes, para-vinyl toluene or mixtures thereof, and the like. The most preferred aromatic vinyl monomer is styrene.

By the term "sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds", it is meant addition polymerizable vinyl or vinylidene monomers corresponding to the formula:



- 20 wherein A<sup>1</sup> is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R<sup>1</sup> is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R<sup>2</sup> is
- 25 independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; or alternatively R<sup>1</sup> and A<sup>1</sup> together form a ring system.

- By the term "sterically bulky" it is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization
- 30 catalysts at a rate comparable with ethylene polymerizations.

Ethylene and alpha-olefins having a linear aliphatic structure such as propylene, butene-1, hexene-1 and octene-1 are not considered to be sterically hindered aliphatic monomers.

Preferred sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl, and the like. Most preferred aliphatic or cycloaliphatic vinyl or vinylidene compounds are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene. Simple linear non-branched  $\alpha$ -olefins including for example,  $\alpha$ -olefins containing from 3 to about 20 carbon atoms such as propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1 are not examples of sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds.

The interpolymers comprising polymer units defined above under i), ii) and iii) can be substantially random, pseudo-random, random, alternating, diadic, triadic, tetradic or any combination thereof. That is, the interpolymer product can be variably incorporated and optionally variably sequenced. The preferred sequence is substantially random. The preferred substantially random interpolymers are the so-called pseudo-random interpolymers as described in EP-A-0 416 815 by James C. Stevens et al. and US Patent No. 5,703,187 by Francis J. Timmers, both of which are incorporated herein by reference in their entirety.

The preferred polyolefin interpolymer are ethylene/styrene interpolymers. Particularly preferred are substantially random ethylene/styrene interpolymers.

The term "variably incorporated" as used herein refers to an interpolymer, particularly an ethylene/styrene interpolymer, manufactured using at least two catalyst systems wherein during interpolymerization the catalyst systems are operated at different incorporation or reactivity rates. For example, the interpolymer product having a total styrene content of 36 weight percent is variably incorporated where one catalyst system incorporates 22 weight percent styrene and the other catalyst system incorporates 48 weight percent styrene and the production split between the two catalyst systems is 47/53 weight percentages.



Representative "pseudo-random" interpolymers are the ethylene/styrene interpolymers described in U.S. Patent 5,703,187, the disclosure of which is incorporated herein in its entirety by reference.

- 5 "Random" interpolymers are those in which the monomer units are incorporated into the chain such that there exist various combinations of ordering including blockiness, e.g. where either the ethylene or the aliphatic alpha-olefin monomer or the sterically hindered vinylidene monomer or both can be repeated adjacent to one another.

- 10 Representative "alternating" interpolymers are, for example, alternating ethylene/styrene interpolymers in which the ethylene and the sterically hindered vinylidene monomer occur in repeat alternate sequences on the polymer chain in atactic or stereospecific structures (such as isotactic or syndiotactic) or in combinations of the general formula  $(AB)_n$ .

- 15 The term "substantially random" as used herein in reference to the interpolymers comprising the above-mentioned monomers i), ii) and iii), and to ethylene/ styrene interpolymers in particular, generally means that the distribution of the monomers of the interpolymers can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in Polymer Sequence Determination, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78, the disclosure of which is incorporated herein by reference. Substantially random interpolymers  
20 do not contain more than 15 mole percent of the total amount of vinyl or vinylidene aromatic monomer in blocks of vinyl or vinylidene aromatic monomer of more than 3 units.

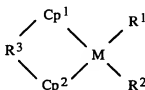
- Preferably, the substantially random interpolymers is not characterized by a high degree (greater than 50 mole percent) of either isotacticity or syndiotacticity. This means that in the carbon-13 NMR spectrum of the substantially random interpolymers, the peak  
25 areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

- A preferred method of preparation of the substantially random interpolymers includes polymerizing a mixture of polymerizable monomers in the presence of one or more  
30 metallocene or constrained geometry catalysts in combination with various cocatalysts, as described in EP-A-0,416,815 by James C. Stevens et al. and US Patent No. 5,703,187 by Francis J. Timmers, both of which are incorporated herein by reference in their entirety. Preferred operating conditions for such polymerization reactions are pressures from

atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in EP-A-514,828; as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635; 5,470,993; 5,703,187; and 5,721,185, all of which patents and applications are incorporated herein by reference.

The substantially random  $\alpha$ -olefin/vinyl aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula



wherein  $\text{Cp}^1$  and  $\text{Cp}^2$  are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other;  $\text{R}^1$  and  $\text{R}^2$  are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxyl groups, or aryloxy groups, independently of each other; m is a group IV metal, preferably Zr or Hf, most preferably Zr; and  $\text{R}^3$  is an alkylene group or silanediyl group used to cross-link  $\text{Cp}^1$  and  $\text{Cp}^2$ .

The substantially random  $\alpha$ -olefin/vinyl aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety.

Also suitable are the substantially random interpolymers which comprise at least one  $\alpha$ -olefin/vinyl aromatic/vinyl aromatic/ $\alpha$ -olefin tetrad disclosed in U.S. Application No. 08/708,869 filed September 4, 1996 and WO 98/09999 both by Francis J. Timmers et al.. These interpolymers contain additional signals in their carbon-13 NMR spectra with

- intensities greater than three times the peak to peak noise. These signals appear in the chemical shift ranges of 43.70 - 44.25 ppm and 38.0 - 38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9, and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70 - 44.25 ppm are methine carbons and the signals in the region 38.0 - 38.5 ppm are methylene carbons.

- It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer insertions preceded and followed by at least one  $\alpha$ -olefin insertion, e.g. an ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an  $\alpha$ -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon-13 NMR peaks but with slightly different chemical shifts.

- These interpolymers can be prepared by conducting the polymerization at temperatures of from about -30°C to about 250°C in the presence of such catalysts as those represented by the formula



- wherein: each  $C_p$  is independently, each occurrence, a substituted cyclopentadienyl group  $\pi$ -bound to M; E is carbon or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, hydrogen, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms; each R' is independently, each occurrence, hydrogen, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to about 30, preferably from 1 to about 20, more preferably from 1 to about 10 carbon or silicon atoms or two R' groups together can be a  $C_1$ - $C_{10}$  hydrocarbyl substituted 1,3-butadiene; M is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. Particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula:



- wherein each R is independently, each occurrence, hydrogen, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30, preferably from 1 to about 20, more preferably from 1 to about 10 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

- Particularly preferred catalysts include, for example, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium dichloride, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium 1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium di-C<sub>4</sub> alkyl, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium di-C<sub>4</sub> alkoxide, or any combination thereof and the like.

- It is also possible to use the following titanium-based constrained geometry catalysts, [N-(1,1-dimethylethyl)-1,1-dimethyl-1-((1,2,3,4,5- $\eta$ )-1,5,6,7-tetrahydro-s-indacen-1-yl)silanaminato(2-)-N]titanium dimethyl; (1-indenyl)(tert-butylamido)dimethylsilane titanium dimethyl; ((3-tert-butyl)(1,2,3,4,5- $\eta$ )-1-indenyl)(tert-butylamido) dimethylsilane titanium dimethyl; and ((3-iso-propyl)(1,2,3,4,5- $\eta$ )-1-indenyl)(tert-butyl amido)dimethylsilane titanium dimethyl, or any combination thereof and the like.

- Further preparative methods for the interpolymers used in the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl<sub>3</sub>) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem., Vol. 35, pages 686-687 [1994]) have reported copolymerization using a MgCl<sub>2</sub>/TiCl<sub>4</sub>/NdCl<sub>3</sub>/ Al(iBu)<sub>3</sub> catalyst to give random copolymers of styrene and propylene. Lu et al. (Journal of Applied Polymer Science, Vol. 53, pp. 1453 to 1460, 1994) have described the copolymerization of thiylen and styrene using a TiCl<sub>4</sub>/NdCl<sub>3</sub>/ MgCl<sub>2</sub>/Al(Et)<sub>3</sub> catalyst.

- Semetz and Mulhaupt, (Macromol. Chem. Phys., Vol. 197, pp. 1071-1083, 1997) have described the influence of polymerization conditions on the copolymerization of styrene with ethylene using  $\text{Me}_2\text{Si}(\text{Me}_2\text{Cp})(n\text{-tert-butyl})\text{TiCl}_2$ /methylaluminoxane Ziegler-Natta catalysts. Copolymers of ethylene and styrene produced by bridged metallocene catalysts have been
- 5 described by Arai, Toshiaki and Suzuki (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem., Volume 38, pages 349-350, 1997; U.S. Patent No. 5,883,213 and DE-A-197 11 339) and in U.S. Patent No. 5,652,315, issued to Mitsui Toatsu Chemicals, Inc.. The manufacture of  $\alpha$ -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene is as described in US Patent No. 5,244,996, issued to Mitsui
- 10 Petrochemical Industries Ltd. or US Patent No. 5,652,315 also issued to Mitsui Petrochemical Industries Ltd, or as disclosed in DE-A-197 11 339 to Denki Kagaku Kogyo KK. All the above methods disclosed for preparing the interpolymer component are incorporated herein by reference. Also, although of high isotacticity and therefore not "substantially random", the random copolymers of ethylene and styrene as disclosed in
- 15 Polymer Preprints Vol. 39, No. 1, March 1998 by Toru Aria et al. can also be employed for the purposes of the present invention.

- While preparing the substantially random interpolymer, an amount of atactic vinyl aromatic homopolymer may be formed due to homopolymerization of the vinyl aromatic monomer at elevated temperatures. The presence of vinyl aromatic homopolymer is in
- 20 general not detrimental for the purposes of the present invention and can be tolerated.

- The substantially random interpolymer usually contains from about 5 to about 65, preferably from about 5 to about 55, more preferably from about 10 to about 50 mole percent of at least one vinyl or vinylidene aromatic monomer; or sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomer; or both; and from about 35 to about 95,
- 25 preferably from about 45 to about 95, more preferably from about 50 to about 90 mole percent of ethylene and/or at least one aliphatic  $\alpha$ -olefin having from about 3 to about 20 carbon atoms.

- The most preferred substantially random interpolymers are interpolymers of ethylene and styrene and interpolymers of ethylene, styrene and at least one alpha-olefin containing
- 30 from 3 to 8 carbon atoms.

The presence of other polymerizable ethylenically unsaturated monomer(s) is optional.

The density of the substantially random interpolymers is generally about 0.930 g/cm<sup>3</sup> or more, preferably from about 0.930 to about 1.045 g/cm<sup>3</sup>, more preferably from about 0.930 to about 1.040 g/cm<sup>3</sup>, most preferably from about 0.930 to about 1.030 g/cm<sup>3</sup>. The molecular weight distribution,  $M_w/M_n$ , is generally from about 1.5 to about 20, preferably from about 1.8 to about 10, more preferably from about 2 to about 5.

Thermoplastic polymers useful in the present invention also include alkenyl aromatic polymers. The alkenyl aromatic polymers may be comprised solely of one or more alkenyl aromatic homopolymers, one or more alkenyl aromatic copolymers, a blend of one or more of each of alkenyl aromatic homopolymers and copolymers, or blends of any of the foregoing with a non-alkenyl aromatic polymer. Regardless of composition, the alkenyl aromatic polymer material comprises greater than 50 weight percent and preferably greater than 70 weight percent alkenyl aromatic monomeric units. Most preferably, the alkenyl aromatic polymer material is comprised entirely of alkenyl aromatic monomeric units.

Suitable alkenyl aromatic polymers include homopolymers and copolymers derived from alkenyl aromatic compounds such as styrene, alpha-methylstyrene, ethylstyrene, vinyl benzene, vinyl toluene, chlorostyrene, and bromostyrene, t-butyl styrene, including all isomers of these compounds. Suitable polymers also include alkenyl aromatic polymers having a high degree of syndiotactic configuration. A preferred alkenyl aromatic polymer is polystyrene. Minor amounts of monoethylenically unsaturated compounds such as C<sub>2</sub>-C<sub>6</sub> alkyl acids and esters, ionic derivatives, and C<sub>4</sub>-C<sub>6</sub> dienes may be copolymerized with alkenyl aromatic compounds. Examples of copolymerizable compounds include acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, acrylonitrile, maleic anhydride, methyl acrylate, ethyl acrylate, isobutyl acrylate, n-butyl acrylate, methyl methacrylate, vinyl acetate and butadiene.

General purpose polystyrene is the most preferred alkenyl aromatic polymer material. The term "general purpose polystyrene" is defined in the Encyclopedia of Polymer Science and Engineering, Vol. 16, pp. 62-71, 1989. Such polystyrene is often called also referred to as crystal polystyrene or polystyrene homopolymer.

The monoalkenyl aromatic polymers may be suitably modified by rubbers to improve their impact properties. Examples of suitable rubbers are homopolymers of C<sub>4</sub>-C<sub>6</sub> conjugated dienes, especially butadiene or isoprene; interpolymers of one or more alkenyl aromatic monomers, and one or more C<sub>4</sub>-C<sub>6</sub> conjugated dienes; interpolymers of ethylene and propylene or ethylene, propylene and a nonconjugated diene, specially 1,6-hexadiene

- or ethylidene norbornene; homopolymers of C<sub>4</sub>-C<sub>6</sub> alkyl acrylates; interpolymers of C<sub>4</sub>-C<sub>6</sub> alkyl acrylates and an interpolymizable comonomer, especially an alkenyl aromatic monomer or a C<sub>4</sub>-C<sub>6</sub> alkyl methacrylate. Also included are graft polymers of the foregoing rubbery polymers wherein the graft polymer is an alkenyl aromatic polymer. A preferred
- 5 alkenyl aromatic polymer for use in all of the foregoing rubbery polymers is styrene. A most preferred rubbery polymer is polybutadiene or a styrene/butadiene copolymer.

Impact modified alkenyl aromatic polymers are well known in the art and commercially available.

- Suitable polymers to be employed as Component (A) also include alkenyl aromatic
- 10 polymers having a high degree of syndiotactic configuration.

Preferred alkenyl aromatic polymers include polystyrene, syndiotactic polystyrene, rubber-modified high impact polystyrene, poly(vinyl-toluene), and poly(alpha-methylstyrene).

- Thermoplastic polymers for use in the present invention also include melt-stable
- 15 lactide polymers or poly(lactide). By "melt-stable" it is meant that the lactide polymer when subjected to melt-processing techniques adequately maintains its physical properties and does not generate by-products in sufficient quantity to foul or coat processing equipment. Lactide polymers are obtainable from lactic acid and may therefore also be referred to as PLA resins. Such lactide polymers are disclosed, for example, in US Patent No. 5,773,562,
- 20 the disclosure of which is incorporated herein by reference in its entirety. Suitable PLA resins are supplied commercially by Cargill Dow under the designation EcoPLA. Poly(lactide) offers the benefits of being a renewable resource material which may be obtained from corn and of being biodegradable (compostable). Thus, poly(lactide) may be disposed of in an environmentally sound fashion.

- 25 The poly(lactide) formulation may include a plasticizer. Suitable plasticizers and selection criteria are disclosed in US Patent No. 5,773,562 (column 14, line 35 – column 15, line 28).

- To improve certain properties of poly(lactide) it may be advantageous to blend a second polymer with the poly(lactide). Suitable 'second polymers' and selection criteria are
- 30 disclosed in US Patent No. 5,773,562 (column 7, lines 21–47).

Suitable elastomers and block polymers include, for example, block copolymers such as styrene/butadiene (SB) block copolymers, styrene/ethylene-but ne/styrene (SEBS)

- block polymers, styrene/ethylene-propylene/styrene (SEPS) block polymers, styrene/isoprene/styrene (SIS) block polymers, and styrene/butadiene/styrene (SBS) block polymers; polyester/polyether block polymers (e.g., HYTEL™); ethylene/propylene rubbers; and ethylene/propylene/diene (EPDM) elastomers. Preferred elastomers are vinyl aromatic/conjugated diene block polymers (e.g. SBS) that have been substantially hydrogenated; that is the block copolymer is characterized by each hydrogenated vinyl aromatic polymer block having a hydrogenation level of greater than 90 percent and each hydrogenated conjugated diene polymer block having a hydrogenation level of greater than 95 percent where hydrogenation converts unsaturated moieties into saturated moieties.
- Also, preferred block polymers have a higher ratio of rigid polymer blocks (e.g. vinyl aromatic polymer blocks) to rubber polymer blocks (e.g. conjugated diene polymer blocks).

Suitable thermoplastic phenoxy resins include polyhydroxyaminoether, polyhydroxyesterether or polyhydroxyether.

- The polymers used in the present invention may be modified, for example, but not limited to, by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art.

- The graft modification of polymers, particularly polyolefins, such as polyethylenes and polypropylenes, with various unsaturated monomers is well known in the art. Such a modification renders an essentially nonpolar material compatible, at least to some limited extent, with a polar material. Graft modification of the polymers is advantageously accomplished by employing an organic compound containing at least one ethylenic unsaturation (e.g., at least one double bond), and at least one carbonyl group ( $-C=O$ ). Representative of compounds that contain at least one carbonyl group are the carboxylic acids, anhydrides, esters and their salts, both metallic and nonmetallic. Preferably, the organic compound contains ethylenic unsaturation conjugated with a carbonyl group. Representative compounds include maleic, fumaric, acrylic, methacrylic, itatonic, crotonic, methyl crotonic and cinnamic acid and their anhydride, ester and salt derivatives, if any. Maleic anhydride is the preferred unsaturated organic compound containing at least one ethylenic unsaturation and at least one carbonyl group.

- The unsaturated organic compound content of the grafted polymer is at least about 0.01 weight percent, and preferably at least about 0.05 weight percent, based on the combined weight of the polymer and the organic compound. The maximum amount of unsaturated organic compound content can vary to convenience, but typically it does not



exceed about 10 weight percent, preferably it does not exceed about 5 weight percent, and more preferably it does not exceed about 2 weight percent. The unsaturated organic compound can be grafted to the polymer by any known technique. The graft-modified polymer may be blended with one or more other polymers, either grafted or ungrafted. For example, a graft modified ethylene-based or propylene-based polymer may be blended with one or more other polyolefins, either grafted or ungrafted, or with one or more polymers other than a polyolefin, either grafted or ungrafted.

The polymers may be sulfonated or chlorinated to provide functionalized derivatives according to established techniques. In addition or alternatively, the polymers may be modified by suitable chain-extending or cross-linking processes using e.g. a physical or a chemical method, including, but not limited to, peroxide-, silane-, sulfur-, radiation-, or azide-based cure systems. A more detailed description of the various cross-linking technologies is described in U.S. Patent No. 5,869,591 and EP-A-778,852, the entire contents of both of which are herein incorporated by reference. Dual cure systems, which use a combination of heat, moisture cure and radiation steps, may be effectively employed. Dual cure systems are disclosed, for example, in EP-A-0 852 596, incorporated herein by reference. For instance, it may be desirable to employ peroxide crosslinking agents in conjunction with radiation, and sulfur-containing crosslinking agents in conjunction with silane crosslinking agents.

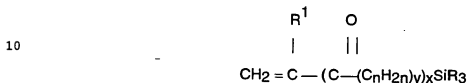
The present invention also provides a film, sheet, or coating, wherein the film, sheet, or coating, the thermoplastic polymeric material or both have been cured, irradiated, or crosslinked. Preferably, the cured, irradiated or crosslinked thermoplastic polymer is a polyolefin, more preferably a polyolefin as defined above, and most preferably an ethylene-based polymer. As used herein, "crosslinking" and "crosslinked" include partially crosslinking (crosslinked) as well as fully crosslinking (crosslinked), as long as the crosslinking results in a gel which is verifiable via ASTM D2765, Procedure A. The various cross-linking agents can be used alone, or in combination with one another.

Suitable heat-activated cross-linking agents include free radical initiators, preferably organic peroxides, more preferably those with one hour half lives at temperatures greater than 120°C. For example, suitable cross-linking agents are organic peroxides, such as 1,1-di-t-butyl peroxy-3,3,5-trimethylcyclohexane, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, t-butyl-cumyl peroxide,  $\alpha,\alpha'$ -di(t-butyl peroxy)-diisopropyl benzene, di-t-butyl peroxide, and 2,5-dimethyl- 2,5-di-(t-butyl peroxy) hexyne. Dicumyl peroxide is the preferred

agent. Additional teachings to organic peroxide cross-linking agents are seen in C.P. Park, *Supra*, pp. 198-204, which is incorporated herein by reference.

Alternatively, polymers may be crosslinked or cured by first grafting a silane onto the polymer backbone and thereafter subjecting or exposing the silane grafted polymer to water or atmospheric moisture. Preferably, the silane grafted polymer is subjected to or exposed to water or atmospheric moisture after a shaping or fabrication operation.

Suitable silanes for silane crosslinking of the polymer, e.g. the ethylene polymer, include those of the general formula



in which R<sup>1</sup> is a hydrogen atom or methyl group; x and y are 0 or 1 with the proviso that when x is 1, y is 1; n is an integer from 1 to 12 inclusive, preferably 1 to 4, and each R independently is a hydrolyzable organic group such as an alkoxy group having from 1 to 12 carbon atoms (e.g. methoxy, ethoxy, butoxy), aryloxy group (e.g. phenoxy), araloxy group (e.g. benzyloxy), aliphatic acyloxy group having from 1 to 12 carbon atoms (e.g. formyloxy, acetyloxy, propanoyloxy), amino or substituted amino groups (alkylamino, arylamino), or a lower alkyl group having 1 to 6 carbon atoms inclusive, with the proviso that not more than one of the three R groups is an alkyl.

Suitable silanes may be grafted to a suitable (ethylene) polymer by the use of a suitable quantity of organic peroxide, either before or during a shaping or fabrication operation. However, preferably, the silane is grafted onto the polymer before shaping or fabrication operations. In any case, the curing or crosslinking reaction takes place following the shaping or fabrication operation by reaction between the grafted silane groups and water. The water permeating into the bulk polymer from the atmosphere or from a water bath or "sauna". The phase of the process during which the crosslinks are created is commonly referred to as the "cure phase" and the process itself is commonly referred to as "curing".

Any silane that will effectively graft to and crosslink the polymer can be used in the present invention. Suitable silanes include unsaturated silanes that comprise an ethylenically unsaturated hydrocarbyl group, such as a vinyl, allyl, isopropenyl, butenyl, cyclohexenyl or  $\gamma$ -(meth)acyloxy allyl group, and a hydrolyzable group, such as, for

example, a hydrocarbyloxy, hydrocarbonyloxy, or hydrocarbylamino group. Examples of hydrolyzable groups include methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, and alkyl or arylamino groups. Preferred silanes are the unsaturated alkoxy silanes which can be grafted onto the polymer. These silanes and their method of preparation are more fully described in US Patent No. 5,266,627 to Meverden, et al.. Vinyl trimethoxy silane, vinyl triethoxy silane,  $\gamma$ -(meth)acryloxy propyl trimethoxy silane and mixtures of these silanes are the preferred silane crosslinkers for use in this invention. If a filler is present, then preferably the crosslinker includes vinyl triethoxy silane.

The amount of silane crosslinker used in the present invention can vary widely depending several factors such as the silane itself, processing conditions, grafting efficiency, organic peroxide selection, the ultimate application, and similar factors. However, typically at least 0.5, preferably at least 0.7, parts per hundred resin (phr) is used. Considerations of convenience and economy are usually the two principal limitations on the maximum amount of silane crosslinker used, and typically the maximum amount of silane crosslinker does not exceed 5, preferably it does not exceed 2, phr.

The silane crosslinker is grafted to the polymer by any conventional method, typically in the presence of a free radical initiator e.g. peroxides and azo compounds, or by ionizing radiation, etc. A suitable grafting method is disclosed in WO 95/29197, the disclosure of which is incorporated herein by reference.

But, for efficient silane grafting, organic initiators are preferred, such as an azo compound or any one of the peroxide initiators, for example, dicumyl peroxide, di-tert-butyl peroxide, t-butyl perbenzoate, benzoyl peroxide, cumene hydroperoxide, t-butyl peroctoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, lauryl peroxide, and tert-butyl peracetate. A suitable azo compound is azobisisobutyl nitrite. The amount of initiator can vary, but it is typically present in an amount of at least 0.04, preferably at least 0.06, phr. Typically, the initiator does not exceed 0.15, preferably it does not exceed about 0.10, phr. The ratio of silane crosslinker to initiator also can vary widely, but the typical crosslinker to initiator ratio is between 10 to 1 to 30 to 1, preferably between 18 to 1 and 24 to 1.

While any conventional method can be used to graft the silane crosslinker to the polymer, one preferred method is blending the two with the initiator in the first stage of a reactor extruder, such as a Buss kneader. The grafting conditions can vary, but the melt temperatures are typically between 160°C and 260°C, preferably between 190°C and

230°C, depending upon the residence time and the half life of the initiator.

Also suitable for the purpose of the present invention are moisture cure silane copolymers, such as ethylene-vinyl silane copolymers and ethylene vinyl acetate-vinyl silane polymers.

- 5 Crosslinking by irradiation may be accomplished by the use of high energy, ionizing electrons (electron beam), ultra violet rays, X-rays, gamma rays, beta particles, controlled thermal heating, or any combination thereof. Electron beam irradiation is preferred. Advantageously, electrons are employed up to 70 megarads dosages. The irradiation source can be any apparatus known in the art such as an electron beam generator operating
- 10 in a range of about 50 kilovolts to about 12 megavolts with a power output capable of supplying the desired dosage. The voltage of the electron beam generator can be adjusted to appropriate levels which may be, for example, 100,000, 300,000, 1,000,000 or 2,000,000 or 3,000,000 or 6,000,000 or higher or lower. In electron beam irradiation, the irradiation is usually carried out at a dosage between about 1 megarads to about 150 megarads,
- 15 preferably between about 3 to about 50 megarads. Further, electron beam irradiation can be carried out conveniently at room temperature, although higher and lower temperatures, for example 0°C to about 60°C, may also be employed. Furthermore, electron beam irradiation can be carried out in air atmosphere, or in reduced oxygen atmosphere or in inert gas atmosphere. Preferably, electron beam irradiation is carried out after shaping or
- 20 fabrication of the article.

- Also, in a preferred embodiment, a polyolefin is incorporated with a pro-rad additive and is subsequently irradiated with electron beam irradiation at about 8 to about 20 megarads. Suitable pro-rad additives are compounds which are not activated during normal fabrication or processing of the polymer, but are activated by the application of
- 25 temperatures (heat) substantial above normal fabrication or processing temperatures or ionizing energy (or both) to effectuate some measurable gelation or preferably, substantial crosslinking.

- Representative pro-rad additives include, but are not limited to, azo compounds, organic peroxides and polyfunctional vinyl or allyl compounds such as, for example, triallyl
- 30 cyanurate, triallyl isocyanurate, pentaerythritol tetramethacrylate, glutaraldehyde, ethylene glycol dimethacrylate, diallyl maleate, dipropargyl maleate, dipropargyl monoallyl cyanurate, dicumyl peroxide, di-tert-butyl peroxide, t-butyl perbenzoate, benzoyl peroxide, cumene hydroperoxide, t-butyl peroxoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butyl

peroxy)hexane, lauryl peroxide, tert-butyl peracetate, azobisisobutyl nitrite and the like and combination thereof. Preferred pro-rad additives for use in the present invention are compounds which have poly-functional (i.e. at least two) moieties such as  $C=C$ ,  $C=N$  or  $C=O$ .

5           At least one pro-rad additive can be introduced to the polymer by any method known in the art. But, preferably the pro-rad additive(s) is introduced via a masterbatch concentrate comprising the same or different base resin as the polymer. Preferably, the pro-rad additive concentration for the masterbatch is relatively high e.g., about 25 weight percent (based on the total weight of the concentrate).

10           Pro-rad additives are introduced to the polyolefin in any effective amount. Preferably, the at least one pro-rad additive introduction amount is from about 0.001 to about 5 weight percent, more preferably from about 0.005 to about 2.5 weight percent and most preferably from about 0.015 to about 1 weight percent based on the total weight of the polymer. Crosslinking can also be promoted with a crosslinking catalyst, and any catalyst  
15           that will provide this function can be used. Suitable catalysts generally include organic bases, carboxylic acids, and organometallic compounds including organic titanates and complexes or carboxylates of lead, cobalt, iron, nickel, zinc and tin. Dibutyltindilaurate, dioctyltinmaleate, dibutyltindiacetate, dibutyltindoctoate, stannous acetate, stannous octoate, lead naphthenate, zinc caprylate, cobalt naphthenate; and the like. Tin  
20           carboxylate, especially dibutyltindilaurate and dioctyltinmaleate, are particularly effective for this invention. The catalyst (or mixture of catalysts) is present in a catalytic amount, typically between about 0.015 and about 0.035 phr.

          The film, sheet, or coating of the invention may also comprise suitable mixtures, such as blends, of thermoplastic polymers. Polymer mixtures or compositions can be  
25           formed by any convenient method. If desired or required, compatibilization between two immiscible or incompatible polymers can be effected by a suitable compatibilizer. Preparing the compositions by physical admixture includes dry blending, melt blending and solution blending, that is dissolving one or both of the components in a suitable solvent, such as for example a hydrocarbon, and combining the components followed by removing the solvent  
30           or solvents. Dry blending involves blending the individual components in solid particulate and subsequently melt mixing in a mixer or by mixing the components together directly in a mixer (for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single

or twin screw extruder including a compounding extruder and a side-arm extruder employed directly downstream of a interpolymerization process.

The mixtures can further be formed *in-situ*. For example, blends comprising a substantially linear ethylene interpolymer may be formed via interpolymerization of ethylene and the desired  $\alpha$ -olefin using a constrained geometry catalyst in at least one reactor and a constrained geometry catalyst or a Ziegler-type catalyst in at least one other reactor. The reactors can be operated sequentially or in parallel. An exemplary *in-situ* interpolymerization process is disclosed in International Application WO 94/01052, incorporated herein by reference. The blends may be prepared using two reactors operated in series or in parallel, or by in-reactor blending using two or more catalysts in a single reactor or combinations of multiple catalysts and multiple reactors. The general principle of making polymer blends by in-reactor blending using two or more catalysts in a single reactor or combinations of multiple catalysts and multiple reactors is described in WO 93/13143, EP-A-0 619 827, and US Patent No. 3,914,362, each of which are incorporated herein by reference. The present polyolefin compositions can be prepared by selecting appropriate catalyst and process conditions with a view to the final composition characteristics.

Thermoplastic polymers suitable for use in the present invention also include recycled and scrap materials and diluent polymers (both encompassed by the expression "diluent materials"), to the extent that the desired performance properties are maintained. Exemplary diluent materials include, for example, elastomers, rubbers and anhydride modified polyethylenes (for example, polybutylene and maleic anhydride grafted LLDPE and HDPE) as well as high pressure polyethylenes such as, for example, low density polyethylene (LDPE), EAA interpolymers, ethylene/vinyl acetate (EVA) interpolymers and ethylene/methacrylate (EMA) interpolymers, and combinations thereof. In some instances, it is preferable for a polymer mixture to contain less than 50 weight percent, more preferably less than 30 weight percent diluent material, particularly when the diluent material is a styrene copolymer, a styrene/butadiene rubber or a styrene/butadiene/styrene block copolymer (SBS).

#### Additives

Optionally, the film, sheet, or coating of the present invention may further comprise additives, including, but not limited to, antioxidants (e.g., hindered phenolics, such as IRGANOX™ 1010 or IRGANOX™ 1076 supplied by Ciba Specialty Chemicals), phosphites (e.g., IRGAFOS™ 168 also supplied by Ciba Specialty Chemicals), cling additives (e.g.,

polyisobutylene (PIB), SANDOSTAB PEPQ™ (supplied e.g. by Ciba Specialty Chemicals), pigments, colorants, deodorants, fillers, plasticizers, medical ornaments such as diaper rash ornaments, UV stabilizers, heat stabilizers, processing aid and combinations thereof.

Although generally not required, the film, sheet, or coating of the present invention may also contain additives to enhance antiblocking (antiblock agents) coefficient of friction characteristics (slip agents) including, but not limited to, untreated and treated silicon dioxide, talc, calcium carbonate, and clay, as well as primary, secondary and substituted fatty acid amides, and combinations thereof.

Still other additives, such as quaternary ammonium compounds alone or in combination with ethylene-acrylic acid (EAA) copolymers or other functional polymers, may also be added to enhance the anti-static characteristics of the film, sheet, or coating of the invention. Enhanced anti-static characteristics promote the usefulness of the inventive film, sheet, or coating in, for example, cushioned packaging of electronically sensitive goods.

#### Films, Sheets, Coatings

The films, sheeting, or coatings used in and according to the present invention are characterized in that they comprise at least one layer, which has a 'fringed' surface microstructure. In this document, a film, sheet, or coating, or a layer thereof having such fringed surface microstructure is also referred to as "fringed film, sheet, coating or layer", including each item individually, e.g. "fringed film". The fringed surface microstructure may cover a desired part or parts, or substantially the entire fringed item, depending on the intended use of said item. When magnified, this fringed surface microstructure is shown to be formed by a broken up base or matrix covered with fibrillar, strand-like or hair-like, spiky aberrations. The base is seen to consist of a pattern of peaks or protrusions separated by troughs or valleys. Irregularly shaped, fine tentacles or fibrils (herein referred to as 'fringes') are protruding from these peaks. The fringes may be seen to have wave-like brims. A particular peak may carry one, two, three, four or more fringes. Peaks with several fringes may have a crown-like appearance. The fringed microstructure of the film, sheet, or coating may only be microscopically visible, for example at an enlargement of at least about 10 times, e.g. using Scanning Electron Microscopy (SEM), or at an enlargement of 40 times to about 100 times, e.g. using optical microscopy. The fringes are substantially solid aberrations, e.g. as opposed to hollow or partially hollow protrusions. This means that the fringes are compact structures substantially entirely filled with and consisting of the thermoplastic material forming the fringed layer, possibly slightly grooved at the top.

The base (of the fringe layer) and the fringes (themselves) are composed of the same thermoplastic polymeric material. The fringes are integral components of the layer forming the fringed surface microstructure.

Suitable parameters to characterize the fringe surface microstructure include for example fringe density and fringe length. Methods to determine these parameters are known in the art, e.g. optical microscopy and preferably scanning electron microscopy (SEM), as well as optical surface profilometry.

The density of individual fringes is at least about 1000 per square centimeter ( $\text{cm}^2$ ), preferably at least about 2000/ $\text{cm}^2$ , more preferably at least about 4000  $\text{cm}^2$ , and most preferably from about 4000 to about 15000 per  $\text{cm}^2$ . If desired, the fringe density may be selected to vary within the fringed surface microstructure. Generally, the length of the fringes depends on (among other things) the ultimate elongation and tensile strength of the thermoplastic polymeric material forming the peaks and fringes.

As used herein, the length of a fringe is the greatest distance between a (base) valley and the tip of a fringe emerging from a peak. The fringes should have a minimum height of at least about 40 micrometers (microns) or more, preferably of at least about 80 microns or more, most preferably of at least about 120 microns or more. Typically, the fringe height is less than about 1 millimeter, preferably less than 600 microns. Most preferably, the fringe height is in the range of from about 200 to about 400 microns.

Another parameter characterizing the fringed surface microstructure is the center-to-center distance between two adjacent fringes. Preferably, the center-to-center distance is from about 100 to about 300 microns.

The particular three-dimensional fringed surface configuration characterizing at least one layer of the film, sheet, or coating according to the present invention may be obtained starting from a suitable precursor film, sheet, or coating. The structure of said precursor is characterized by a distinct surface texture consisting in a pattern of different (surface) thicknesses, i.e. areas of reduced thickness (valleys or troughs) and areas of greater thickness (peaks or protrusions). Advantageously, this pattern is predetermined and may be irregular or regular.

Alternatively, the precursor may be a foamed structure, e.g. a film, sheet, or coating having a foamed surface layer. In such case, the precursor protrusions are formed by the microbubbles of the foam.



In the following, a film, sheet, or coating characterized by such pattern of different surface thicknesses and suitable to give a fringed surface microstructure will be referred to as "precursor" (film, sheet, or coating). This includes a film, sheet, or coating which in part is characterized by such pattern of different surface thicknesses. The protrusions of the precursor surface are understood to be essential for the formation of the fringed surface microstructure in that such microstructure cannot readily be obtained from a regular smooth film. For example, it was found that brushing of a smooth surface, e.g. of a basic film, sheet, or coating according to the techniques described hereinbelow does not result in the desired regularly fringed surface quality.

Advantageously, the height of the protrusions is at least about 20 microns, preferably at least about 50 microns and most preferably at least about 80 microns. The height of the protrusions should be less than about 1 mm. Preferably, the height of the protrusions is in the range of from about 60 microns to about 500 microns, more preferably in the range of from about 80 microns to about 300 microns. Advantageously, the protrusions have a flattened or rounded top relative to the spiky ends of the fringes, edged structures are also suitable to form fringes. Preferred are protrusions in the form of knobs, naps, bumps or truncated cones. Generally, the shape of the peaks or protrusions is affected by the viscosity of the thermoplastic polymeric material forming the peaks or protrusions.

To obtain the fringed surface microstructure the protrusions on the precursor surface are deformed such that they are essentially longitudinally and permanently extended. Deformation should be at least to, preferably beyond the yield point of the polymer forming the protrusions. Preferably, such extension is the result of treatment using mechanical means. Advantageously and preferably, the fringes are obtained by stretching the protrusions by a factor of about two to about four. Stretching by a factor of below 2, e.g., by a factor of at least 1.1 may also provide the desired result. Stretching by a factor of e.g. 2 means that a protrusion which is 100 microns high is extended to a fringe length of 200 microns. As compared to the precursor, the fringed surface microstructure provides a substantially enlarged surface area.

For example, mechanical deformation suitable to create a fringed surface microstructure in accordance with the present invention may rely on the principle of friction and involve the use of an abrading device which has a harder surface or surface coating than the polymer surface to be treated. Suitable abrasives include, but are not limited to,

sandpaper or sand-paper type materials, brushes, steel wool, or abrasive fabrics, such as a fleece or a non-woven having the required surface hardness. Suitable materials for the brush are, for example, nylon, glass-fiber or metal wire, such as bronze. It is readily apparent to the person skilled in the art that the number (density) and length of the fringes is affected by the type of abrasion material and the particular technique of treatment therewith. Critical parameters include deforming speed, applied pressure, temperature, particularly the polymer surface temperature, and hardness (difference). While any form of deformation movement may create a fringed surface microstructure, best results are obtained by circular, oscillating or linear movements, or any combination thereof. The general direction of these movements relative to the film surface and film orientation may be longitudinal, transverse, angled, or any combination thereof. If the treatment is essentially unidirectional, it is preferred to have at least two consecutive steps of either unidirectional or angled treatment. In the case of rotational or oscillating treatment, sequential treatment steps can improve the final quality of the surface. For each combination of surface hardnesses, i.e. surface hardness of the abrasion material and surface hardness of the polymer surface, exists an optimum type of movement and speed to obtain a particular fringed surface microstructure, e.g. fringe length and density. Such optimization is within routine experimentation. When magnified, e.g. using the SEM technique, the tops of the walls of the craters may be seen to be frayed, torn and elongated.

The mechanical treatment of the precursor may be performed in an in-line or an off-line process.

The precursor film, sheet, or coating may be produced using conventional methods. The precursor film may be uniaxially or biaxially oriented.

Generally, a film can be made by any known process including, but not limited to, solvent casting (for example, dispersion in a solvent, solvent including an aqueous medium extrusion (for example, blown or casting), compression (for example, molding), roll milling or calendaring, or any combination thereof. Extrusion as used herein is intended to include coextrusion, extrusion coating or any combination thereof. One or more films may be laminated to form a multilayer structure. The film may be oriented after forming using known techniques and equipment, such as tenter frame, double bubble or trapped bubble orientation techniques. One or more layers of the film may be expanded, for example with a conventional blowing agent, to make a foamed film. To make foamed film structures or layers, either physical or chemical blowing agents may be used to achieve suitable foam

- densities, e.g. foam densities from 1 g/cc to as low as 0.01 g/cc. Suitable blowing agents are known in the art. The foams may be open or closed cell, according to ASTM D2856. The cell sizes of the foams typically are from about 0.01 mm to about 5.0 mm, preferably from about 0.02 to about 2.0 mm. The foams may be crosslinked or non-crosslinked. As
- 5 mentioned above, the fringed surface microstructure may be formed by mechanical treatment of a foamed surface.

A sheet can be made by any known process including, but not limited to, solvent casting, extrusion, roll milling, compression or calendering or any combination thereof.

- A coating can be made according to methods known in the art, e.g. by extrusion
- 10 coating or involving a roller and doctor blading.

- For example, a process suitable for making a precursor film, sheet or coating may comprise extruding a thermoplastic material in a molten state onto a moving belt or a roller surface which presents a negative or reverse structure with respect to the desired surface texture such that the thermoplastic material closely contacts said reverse structure.
- 15 Advantageously, the surface temperature of the moving belt or roller is adjustable. The negative structure may, for example, consist of very fine cavities. Preferably, the process conditions are such that the cavities are essentially completely filled by the thermoplastic material. This may be achieved by proper selection of the thermoplastic material, e.g. a polymer having a low viscosity, and/or proper selection of the temperature of the polymer
- 20 mass, and/or by exposing the cavities to a vacuum such that the air is removed. Advantageously, the polymer mass filling the cavities is about at or above the Vicat softening point. The thermoplastic material is solidified so as to adopt a surface texture which represents the positive counterpart of the negative structure of the moving belt or roller surface and thus form the desired precursor. After solidification, the precursor is
- 25 removed from the roller or moving belt surface and subjected to further mechanical treatment suitable to create the fringed surface microstructure, e.g. treatment as described above. A process suitable to prepare a precursor structure is disclosed in WO 97/02128, which is incorporated herein by reference.

- A good fringed surface quality may also be obtained by allowing the molten polymer
- 30 to fully solidify on the matrix roll during the surface shaping, meaning that more than about 90 % of the polymer is cooled well below the Vicat softening point. A compression molding process suitable to make the fringed surface structure used in the present invention is disclosed in WO 00/16965, which is incorporated herein by reference with respect to the

process and devices described therein. Preferably, the process does not involve the application of a vacuum.

Suitable equipment for such continuous compression molding process to make a fringed film, sheet, or coating comprises a set of surfaces, as presented for example by a pair of rollers, preferentially enabling temperature control, with defined surface qualities. The surfaces may have different, similar or equal surface roughness and shape. The surfaces may be part of the primary equipment used to make the (base) film, sheet, or coating (in-line process), or be installed for a secondary compression molding process off-line. At least one surface, hereinafter referred to as matrix surface, is characterized by the presence of numerous cavities with a projected area of at least about 1000 square microns and a depth of at least about 100 microns. Such matrix surface structure can be provided by a porous material, such as cast irons, an open cell, foamed material, by woven or entangled fibrous structures (e.g., natural, metallic, polymeric), by sintering of a suitable material, such as metallic, ceramic, polymeric or natural particles, or fibrous materials, by mechanical or chemical treatment of a suitable material, or by eroding techniques (electrical, chemical, lasering). Suitable techniques and technologies are known in the art. Such matrix surface is applied on a device suitable for processing a film, sheet, or coating, such as a roller or a belt. Typically, the angle of the cavities relative to the matrix surface will be in the range of from about 45 to about 90 degrees.

To prepare the desired precursor having a pattern of different surface thicknesses a polymer mass, e.g. in the form of a polymer melt, polymer dispersion, polymer suspension, polymer solution, film, sheet, or coating is applied on the matrix surface. Advantageously and preferably, the polymer mass is applied in form of a solid semi-finished product, in particular in form of a film, sheet, or coating. If desired, lamination (to that surface of the semi-finished product which is not facing the matrix surface) may be accomplished simultaneously with the surface modification step. The mechanical properties of the semi-finished product will not essentially deteriorate or be substantially affected in the compression molding process.

One or more counter surfaces suitable to apply pressure onto the polymer mass, such as roller or belts, are used to force the polymer mass into the cavities of the matrix surface. Preferably, penetration of the polymer mass into the cavities is facilitated by heating the surface of the mass to a temperature which is at or above the Vicat softening point. The surface of the polymer mass is molded such that individual, distinct surface

elevations or protrusions are formed in the cavities, thus yielding a suitable precursor structure. At the same time, the other surface of the polymer mass is shaped according to the structure of the counter surface of the pressuring device. The surfaces of the precursor reflect the surface characteristics of both rolls, the pressure roll and the matrix roll. Low viscosity of the polymer material filling the cavities is preferred.

After the surface molding, the film, sheet, or coating is released from the matrix surface which step requires sufficient web strength to pull the molded elevations out of the cavities. Sufficient web strength is achieved by appropriately cooling the precursor, if desired using additional external cooling sources, such as an air knife or cooling water. The fringe layer temperature and line speed should be adjusted to achieve minimal or no drawing of the polymer during removal from the matrix surface, and minimal to no adhesion to the cavity walls.

The tensile strength of the precursor may be enhanced by support layers. If the polymer mass fed into the compression molding equipment is a suspension or emulsion (additional) drying and/or curing and/or cross-linking may be performed on the matrix roller or belt, optionally in the presence of additional sources of energy for curing or crosslinking after the surface molding has occurred. Optionally, the fringed film, sheet, or coating thus obtained may be subjected to further mechanical treatment, e.g. with an abrasive device.

In order to avoid sticking of the film, sheet, or coating according to the invention to the equipment used in making said item or to facilitate release of the item, it may be desirable to use a sacrificial backing layer or protective layer. The sacrificial layer can be, but not limited to, oriented or non-oriented PET film, aluminum foil, non-woven/fleece, oriented or non-oriented polypropylene film, oriented or non-oriented polystyrene film, oriented or non-oriented PLA (polylactic acid) film, or natural fiber substrates, and/or a 'release aid', such as PTFE, silicon, etc. as equipment coating materials (e.g. on the pressure roll or counter roll), or plasticizer or migratory additives in the polymer matrix (fatty acids, etc.). Film or sheet exhibiting a melting point which is at least 20°C higher than the fringed layer material are suitable as sacrificial layers.

Advantageously and preferably, the thermoplastic polymer or polymer blend forming the fringed surface microstructure is selected such that the fringes (after formation) are dimensionally stable, resilient and resistant to deformation under load at ambient temperature. Generally, polymer selection will be dictated by the particular process conditions for making the precursor and the fringed surface and the specific performance

requirements of the envisaged end-use applications. Optimal filling of the cavities with the polymer is favored by employing a thermoplastic having a low viscosity at the relevant processing temperature.

- 5 Fringed films, sheets, or coatings, and articles of manufacture comprising such fringed film, sheet or coating particularly benefit from the fringed surface microstructure. Performance attributes which can be specifically provided or enhanced by the fringed surface microstructure include soft, velvety and textile-like feel or touch, matte appearance, liquid repellency, anti-skid and good grip properties, surface variability and surface
- 10 imprintability, controlled release properties, storage capabilities, and protective properties. Depending on the intended end-use application the fringed surface microstructure can be designed and optimized to specifically exploit or favor one or more of these performance attributes, for example by selection of a proper polymer material or polymer materials, and/or of a proper fringe structure. If desired or required, the fringed film, sheet or coating may be made to provide additional functional properties, such as breathability, increased
- 15 heat resistance, or barrier properties.

- The present invention also relates to an article of manufacture made from or comprising a fringed film, sheet or coating. Based on the specific advantageous performance attributes afforded by the fringed surface microstructure such articles of manufacture are useful, for example, for decoration or as decorative materials, for
- 20 packaging or as packaging material, for use as labels or signs, in automotive applications, for industrial, personal or medical hygiene applications, for apparel or protective clothing, and for household applications.

- More specifically, the fringed surface microstructure characterizing the articles of the invention can be designed to afford an excellent soft, velvety and textile-like feel or touch.
- 25 The fringed film, sheet, or coating may show excellent haptics and be very pleasant and easy on a person's skin. Based on this property such fringed film, sheet, or coating is useful to manufacture plastic based articles used in soft touch, soft feel applications. For example, soft touch, soft feel materials are desirable in the automotive industry, for example on automotive interior surfaces, including but not limited to instrument panels, console liners,
- 30 door panels, seat covers, headliners, and steering wheel covers. The fringed films, sheets, or coatings according to the invention are also useful to make decorative fabrics or articles with (direct) skin contact, for example, furniture covers including outdoor furnishing, such as desk covers, cushions, including patio air cushions, drapes, bedspreads, and table cloths;

ostomy bags; mattresses including air mattresses; life vests; artificial leather (replacement); floor covering; medicinal and personal hygienic articles, including for example bandages, band aids, condoms, incontinence articles, such as diapers, or parts thereof including e.g., top sheet, ears or wings, cuffs, side panels, and back sheets; (disposable) garments

5 apparel, and protective gear; such as medical drapes and gowns, athletic clothing, raincoats, hats and caps; grip bands; (bag) handles; linings, for example for luggage, bags or handbags, or shoes; gloves, and protective gear, artificial skin, skin imitations, toys, industrial hygienic articles, such as wipes or disposable toilet seat covers, head rest covers and the like. For end-use applications requiring a soft feel the fringe length is

10 advantageously at least about 150 microns or more. Generally, use of polymers having a low modulus polymer will be advantageous to obtain a soft feel. The use of polymers having a higher modulus will result in differentiated haptics and tactility, affording a (relatively) rough feel rather than a soft feel. Articles with a fringe surface microstructure based on a polymeric material having a higher modulus can be useful, for example, as scouring or

15 abrading devices, or to provide anti-skid performance.

Another benefit provided by the fringed surface microstructure is a matte (mat) appearance and further reduced gloss (relative to the precursor). Gloss is determined according to ASTM D-2457. The films, sheets, or coatings according to the invention are useful to manufacture articles relying on excellent aesthetics and matte optical appearance

20 including, for example, decorative overlays, including wall, floor, or ceiling covering products; artificial flowers; linings of jewelry boxes and luggage; anti-glare surfaces such as billboards and window cling signs, merchandise bags, and projection and movie screens.

Another advantageous property characterizing the fringed film, sheet, or coating is a differentiated surface tension, as determined by the test methods according to ASTM D-2578 or DIN 53364, and water contact angle. The fringed films, sheets, or coatings are

25 useful for applications and articles where surface water or liquid drain management, e.g. such that water beads up and drains off, is required. Such applications and articles include, for example, clothing with liquid repellant surfaces, e.g. rain gear, such as hats, coats, or ponchos, protective clothing, feminine hygiene top sheet, (disposable) table cloth and

30 shower curtains.

Furthermore, the fringed surface microstructure also provides a frictional behavior, as reflected e.g. in the dynamic coefficient of friction, which affords anti-slip or anti-skid and better grip performance attributes to a fringed film, sheet, or coating, or an article of

manufacture with a surface made from or comprising a fringed film, sheet, or coating of the invention. The dynamic coefficient of friction of a particular fringed surface may be determined according to ISO 8295, relative to various surfaces of interest, including, for example, the same or a different fringed surface, or a glass, metal, ceramic or polyolefin surface. The fringed surface microstructure provided herein typically provides an increased coefficient of friction as compared to non-fringed (plain) film of the same composition. The better grip and anti-slip properties make the fringed film, sheet, or coating useful for a variety of applications and articles including, but not limited to floor cover backings, furniture covers, gloves, table wear, bathroom articles, such as shower shoes and shower mats, roofing, tarps for construction, truck bed covers, box coatings, serving trays (e.g. as used in air planes or restaurants), grip bands or tapes, and non-skid operation room table cover.

The process for making gloves comprises dipping hand forms into a suitable dispersion, such as latex. The hand forms are cleaned, rinsed and dried. Subsequently, the forms are heated and a coagulant for the latex is added to support curing of the latex. The latex is applied to the forms by dipping the forms into the latex bath. Before the product is cured any undesirable solvents or materials are allowed to leach out during a leaching step. The gloves may be removed from the form by blasting them off by air, which is rather difficult to accomplish, or by peeling the latex off the form while inverting it at the same time. Prior to the curing or leaching steps, the gloves may be dipped into a bath for coating with another material. For example, the coating may serve to enhance grippage, increase the wearer's ability to hold onto slippery or wet instruments or improve the feel against a person's skin. The continuous compression molding process according to the present invention can advantageously be used to make gloves with a fringed surface microstructure. In such process, the forms are employed as matrix surface. The peel/inversion process to remove the gloves from the form is applied such as to give the fringed surface microstructure. Thus the secondary dipping step of the conventional process becomes redundant.

Another benefit afforded by the fringed surface microstructure is surface variability, particularly surface printability or imprintability (embossing), as reflected in the possibility to create distinct areas of different topography, e.g. using suitable impression techniques. The fringed surface may be (im)printed with or without ink. Printability may be evaluated in terms of ink adhesion, color density (vividness), print definition employing suitable methods known in the art, including for example adhesive tape peel tests, abrasion tests, or simply visual appearance. The ink may reside between the fringes as well as at the tips of the fringes.



Acceptable ink adhesion is possible for water based and solvent based inks and should be selected based on the fringe layer polymer. Color density may vary dependent on the angle of view thus creating a unique 3D-type appearance. Clear fringed film may be reverse printed, e.g. by printing the fringed microstructure and viewing from the reverse side.

- 5           Using, for example, a hot stamp, hot air or friction to re-melt and/or compress part of the fringes in a selected regular or irregular pattern to form a smooth surface, haptic and/or optic effects are achieved by the resulting difference in surface structure and appearance. Thus printing effects may be obtained without the need for color or ink. If the difference in surface structure is marked, it may also be noticeable by a person with reduced visual ability
- 10 or a blind person. Nevertheless, color or ink may be added to enhance the effects.

- The desired imprinting effects may be realized relying on the same principles used in printing or sealing. For example, a stencil or print negative which is a metal or thermoset material that can be heated without distortion to temperatures above the melting point of the thermoplastic polymer forming the fringes may be employed. Suitable temperatures for
- 15 polyethylene are in the range of from about 50°C to about 200°C, preferably from about 60°C to about 160°C, more preferably from about 70°C to about 120°C. The image or pattern of the stencil or print negative is applied by pressing it on the fringed surface such that a three-dimensional effect is obtained. The effects are also obtainable in a process which does not involve contacting the fringed surface, e.g. by applying a jet of hot effluent
- 20 (e.g. air) similar to an air brushing printing process. Another process suitable to obtain imprinting effects is to abrade the fringes on the surface by a mechanical process and thus create areas of differentiated topography resulting in print-like images. Alternatively, to obtain the described effects, the fringed surface may be created only on parts of the basic film, sheet, or coating 'a priori'.

- 25           The fringed surface microstructure can be printed with ink and resist ink from being scratched or abraded, thus enhancing the durability and appearance of the fringed article or item. The benefit of enhanced abrasion and scratch resistance is also afforded to coatings, such as barrier coatings, or metallization. By making the (barrier) coatings or deposits more scratch and abrasion resistant their particular properties will be maintained for a longer
- 30 period of time. The advantage of improved scratch resistance also applies to printed or painted surfaces, e.g. in an automobile, such as dash boards, instrument panels etc., metallized films, e.g. used in the packaging of food, medical items or electronics, and barrier coated films.

Based on its surface variability and/or imprintability the fringed film, sheet, or coating of the present invention is particularly useful to make novelty balloons, book covers, wrapping paper, floor covering, ceiling covering or wall covering, labels, including, for example, in-mold labels and stretch labels, e.g. for bottles, bill boards, or paperboard coatings, e.g. for drinking cups, greeting cards, and party articles.

The increased surface area of the fringed film, sheet, or coating affords enhanced carrying, capturing or storing properties, which can be exploited for numerous applications and articles, including but not limited to articles comprising a controlled release system. For example, such system may provide for the controlled release of antibiotics and may be useful e.g. in wound covers or shower curtains, the controlled release of fragrances or the controlled release of drugs. Enhanced carrying, capturing or storage properties can also be exploited in wipes, tissues, carrier substrates for catalysis, filtration media, diaper top sheets, e.g. coated with diaper rash ointments, anti-static sheets, anti-fog films, and for HF weldability, thermal insulation, sound deadening, meat packaging and poultry diapers. The fringes are suitable structures, which other substances can be embedded into or coated onto. Such structures may allow, for example, the gradual diffusion or the controlled release of substances, such as drugs or fragrances. Such structures may be useful e.g. in transdermal drug delivery systems, fragrance delivery systems, such as soft packages for cosmetics or perfumes, or scented wall covering, or as filtration systems. A porous membrane may be put over the top of the structures to allow the soft surface to breathe to the skin (drugs) or air (fragrances). If a barrier, for example made from SARAN™ or EVOH resin, is coated over the top of the reservoirs and the base of the film is made from a porous material the drug is delivered through the base polymer. Emollients or salves can be placed between or on the fringes to maintain moistness for burn wounds or for diaper rash creams with the soft side against the skin. Antibacterial agents can be placed on the fringed surface to prevent mold and mildew formation, e.g. in shower curtains. Placing a static charge on the surface further enhances the ability to pick up substances, such as dirt or dust.

Furthermore, absorbent materials can be coated onto the fringed surface or be incorporated into the polymer (as a type of filler) before the fringed film, sheet, or coating is made, for example in order to enhance the absorption of coatings or ink. Examples of suitable absorbent fillers include, for example, superabsorbents used in hygiene applications, talc and calcium carbonate.

The fringed film, sheet, or coating may be made to be (moisture) vapor permeable or breathable. For example, breathable films include filled and stretched microporous films, or monolithic films, for example made from a thermoplastic polyurethane, a copolyesterether thermoplastic elastomer, a copolyesteramide thermoplastic elastomer or another highly water vapor transmitting polymer, such as a polyamide. A (thin) fringed layer may be coextruded on top of a previously stretched microporous layer or the fringed film can be stretched. A (thin) fringed layer can also be extruded on top of an inherently breathable monolithic layer. Water vapor breathability is a performance attribute desired or required for use of the fringed film, sheet, or coating of the invention in apparel, such as protective clothing, or in hygienic articles, such as (diaper) backsheet.

For example, a breathable monolithic fringed film is characterized by a high water vapor transmission rate (WVTR) and has a soft touch. In conventional breathable films, the soft touch has been provided by laminating a non-woven to the film. If desirable, the breathable monolithic fringed film may be laminated to another material which provides a different function in the composite, such as noise reduction or elastic recovery. Advantageously, the fringed surface microstructure is designed so as to provide the desired water repellency performance or liquid impermeability. Thermoplastic polymers suitable to make (inherently) breathable fringed film include, for example, polyether block copolymer (e.g., PEBAX™ copolymer), and thermoplastic polyurethane (e.g., PELLETHANE™ polymer). The films may be mono-layer or multi-layer structures, preferably each layer having a high WVTR. The WVTR measured at 38°C and at 90% relative humidity (using ASTM method E96) should be in the range of 500 to 10,000 g/m<sup>2</sup>/day, more typically in the range of 1000 to 6500 g/m<sup>2</sup>/day. Such film is suitable for apparel or other applications for which breathability is desirable, including athletic wear, side panels in diapers or adult incontinence products.

The fringed films, sheets, or coatings are useful for packaging applications, e.g. packaging applications requiring enhanced protection, e.g. against scratching, packaging applications requiring cushioning, and/or printability. Exemplary packaging applications include pouches, e.g. pouches for flowable materials, such milk or detergent pouches, bags, e.g. boutique bags, and protective covers, e.g. for cars, bikes or boats. Fringed film, sheet, or coating comprising poly(lactide) are particularly suitable for disposable articles.

The fringed film, sheet or coating may be elastic. The elastic film of the invention comprises a material which is highly stretchable and which reverts to its original or nearly

original form upon release of any pressure or force applied to the film material. In a preferred embodiment, the elastic film, sheet or coating of the invention achieves at least about 50 percent of its stretched length after the first pull and after the fourth pull to 100% strain (doubled the length). Recovery refers to a contraction of a stretched material upon

5 termination of a force following stretching of the material. Percent recovery may be expressed as:  $[(\text{maximum stretch length} - \text{final sample length}) / (\text{maximum stretch length} - \text{initial sample length})] \times 100$ . Elasticity can also be described by the "permanent set" of the film. Permanent set is the converse of elasticity. A film is stretched to a certain point and subsequently released to the original position before stretch, and then stretched again.

10 The point at which the elastic material begins to pull a load is designated as the percent permanent set. Elastic polymeric materials include, for example, AB and ABA block or graft copolymers (where A is a thermoplastic endblock such as, for example, a styrenic moiety and B is an elastomeric midblock derived, for example, from conjugated dienes or lower alkenes), chlorinated elastomers and rubbers, ethylene propylene diene monomer (EDPM)

15 rubbers, ethylene-propylene rubbers, thermoplastic polyurethanes, ethylene-alpha olefin copolymers, specifically at a density less than 0.89 g/cc, and ethylene-styrene interpolymers with a styrene content of less than 40 weight percent. Blends of these polymers alone or with other modifying elastic or non-elastomeric materials are also contemplated being useful in the present invention. The low modulus of elastic films is also advantageous in terms of

20 haptics.

In a post-treatment step, the fringed film, sheet or coating according to the invention may be uniaxially or biaxially oriented according to methods known in the art.

If desired, the fringed film may be further treated (post treatment) and the surface characteristics of a fringed film may be modified by techniques known in the art, including,

25 for example, corona treatment. Corona treatment increases the polarity of the surface, thus increasing the wetting tension. The greater the polar component the more actively will the surface react with different polar interfaces.

A mono-layer film, sheet, or coating, or articles of manufacture comprising such film, sheet, or coating, may be characterized by a fringed surface microstructure on one side, or

30 on both sides. The fringed microstructure may cover parts of the surface, or the entire surface. Such mono-layer structure is preferably made from a suitable thermoplastic polymeric material indicated as being preferred herein-above. The mono-layer may be made from a single thermoplastic polymer, preferably an ethylene-based polymer, including

for example a heterogeneously or, preferably, a homogeneously branched ethylene polymer, and a substantially random ethylene/styrene interpolymer, a polypropylene polymer, or a (poly)lactide, or a mixture or blend of thermoplastic polymers, preferably comprising the polymers indicated as being preferred. For example, a suitable polymer blend may be composed of two homogeneously branched ethylene-based polymers.

The present invention further provides a mono-layer or multi-layer film, sheet, or coating comprising a thermoplastic polymeric material, wherein the film, sheet, or coating, the thermoplastic polymeric material or both have been cured, irradiated or cross-linked. Advantageously, curing, irradiation or crosslinking is performed after forming of the fringed surface microstructure. Preferably, the cured, irradiated or cross-linked thermoplastic polymer is a polyolefin, most preferably an ethylene (inter)polymer. Crosslinking is achieved using the methods and techniques described in more detail herein-above. Such film, sheet, or coating affords the benefit of enhanced heat resistance, as required, for example, by applications in the automotive industry, such as automotive interior applications, such as steering wheel covers, or articles with much exposure to the sun, such as outdoor furniture cushion covers.

Generally, in a multi-layer film, sheet, or coating according to the invention, at least one layer has a fringed surface microstructure and is comprised of a thermoplastic polymer as defined herein. The fringed microstructure may be present on one or both sides of said layer or layers. The fringed layer may be an inner and/or, an outer layer. A multi-layer film, sheet or coating wherein the fringed layer is an outer layer is preferred.

In a multi-layer structure, each layer will serve a particular function or provide some characteristic to the overall structure. The composition of these layers is chosen depending on the intended end use application, cost considerations, and the like.

For example, layers may serve to provide particular structural or functional characteristics, e.g. add bulk to the structure, promote interlayer adhesion, provide barrier properties, thermal properties, optic properties sealing characteristics, chemical resistance, mechanical properties, or abuse resistance. An adhesion promoting interlayer is also referred to as a tie layer. If a barrier layer is desired or required for the intended end use application, it is selected so as to meet the targeted degree of gas or moisture (im)permeability.

Various materials can be used for these layers, with some of them being used in one or more than one layer in the same film structure. Suitable materials include, for example,

nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, LLDPE, HDPE, LDPE, graft adhesive polymers, such as maleic anhydride grafted polyethylene.

For example, a gas barrier layer may be made from vinylidene chloride copolymer, EVOH copolymer or SARAN™.

Examples of thermoplastic polymers appropriate for use in the seal layer include LLDPE, ULDPPE, VLDPE, POP, EVA copolymer, EAA copolymer and ionomers.

Thermoplastic polymers for use in the bulk layer are advantageously chosen based on cost considerations and include recycled materials. Representative polymers are, for example, LLDPE, such as ethylene/butene copolymers, LDPE, EVA copolymer, (recycled) HDPE, polypropylene polymers and blends thereof.

Examples of thermoplastic polymers appropriate for use in a layer providing advantageous mechanical properties include, for example, ethylene/C<sub>4</sub>-C<sub>8</sub> copolymers. The fringed multi-layer structures according to the invention typically consist of from two to seven layers. Preferred are multi-layer films having three or more layers.

Permeability may be provided by a porous membrane.

For example, it is within the scope of the present invention to provide a multi-layer film, sheet, or coating including the following general two-layer and three-layer structures, wherein the respective compositions of the layers are chosen from thermoplastic polymer resins which provide the requisite functional properties:

Fringed/Bulk  
Fringed/Seal  
Fringed/Adhesion  
Fringed/Bulk/Seal  
Fringed/Bulk/Adhesion  
Fringed/Mechanical/Seal  
Fringed/Mechanical/Adhesion  
Permeability/Fringed/Barrier

For each of these general structures, further internal or external layers may be added to promote inner layer adhesion or add bulk, as appropriate.

The present invention also relates to the use of fringed film, sheet or coating in geomembranes.

Furthermore, the present invention relates to the use of a fringed film in medical ostomy bags, urological collection bags and other liquid containment pouches.

- 5 Furthermore, the invention relates to medicinal collection bags, such as ostomy bags, urological collection bags and other liquid containment bags or pouches comprising a fringed film, particularly a multi-layer coextruded fringed film. The fringed surface microstructure is particularly advantageous and desirable for bags that are worn by a person and are in contact with his or her skin. Ostomy bags and urological collection leg  
10 bags are examples of patient-worn bags. In many commercial applications today, barrier films are combined with soft nonwoven textiles, such as spunbonded or meltblown polyolefin or polyester nonwovens, to provide a laminate structure that can provide patient comfort when worn in contact with the body. The use of fringed film to impart soft "nonwoven" or textile-like feel to a coextruded barrier film structure can result in elimination  
15 of a separate nonwoven textile from a laminated bag structure.

- Of particular interest for incorporation of a fringed film are coextruded barrier films that provide good oxygen, carbon dioxide and odor barrier properties. Barrier properties can be achieved by use of conventional barrier polymers such as polyvinylidene chloride (PVDC, such as SARAN® resin from The Dow Chemical Company), ethylene-vinyl alcohol  
20 (EVOH, such as EVAL® resin from EVAL Company of America), nylon or amorphous nylon (such as GRILON® or GRILAMIDE® resin from EMS-Chemie, CAPRON® nylon from Allied Chemical or MXD6® nylon from Mitsubishi Gas Chemical Company), polyester (PET and PETG, such as EASTAR® polyester resins from Eastman Chemical Company) or phenoxy (such as BLOX® thermoplastic epoxy resins from The Dow Chemical Company). In  
25 producing a coextruded barrier film, it is desired to provide outermost film layers that provide strength and sealability, such as with polyolefin resins. Suitable polyolefin resins include low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), metallocene or plastomer polyethylene (mPE), ethylene-styrene interpolymers (ESI), ethylene-vinyl acetate (EVA), ethylene methyl acrylate (EMA),  
30 ethylene-acrylic acid (EAA), and polypropylene homopolymer (PP) or polypropylene copolymer (coPP), chlorinated polyethylene (CPE), thermoplastic polyurethane (TPU), styrenic block copolymers such as styrene-butadiene-styrene (SBS) and styrene-ethylene-butylene-styrene (SEBS). These resins typically have poor affinity for and adhesion to the

various barrier resins, necessitating the use of suitable tie layer resins to bond the layers together. Tie layers may include polyolefin copolymers that are polar monomer modified, such as ethylene copolymers with 1 to about 40 weight percent of polar comonomer. Suitable ethylene copolymers include EVA, EMA, EAA, ethylene-n-butyl acrylate (EnBA), and maleic anhydride (MAH) grafted polyolefins such as PE-graft-MAH, PP-graft-MAH and EVA-graft-MAH. These resins typically have 0.05 – 1.4 weight percent MAH grafted onto the polyolefin polymer.

Barrier films of the present invention are typically about 1.0 mils (25  $\mu\text{m}$ ) to about 10 mils (250  $\mu\text{m}$ ) in thickness, and preferably about 2.0 mils (50  $\mu\text{m}$ ) to about 6.0 mils (150  $\mu\text{m}$ ) in thickness. Thicknesses significantly greater than the preferred range can result in ostomy bags or collection bags that are stiff and inflexible, resulting in poor conformation to a patient's body. This results in uncomfortable wearing of the bag, as well as aesthetically unacceptable bulging or protrusion of the bag from under the patient's clothing, eliminating the discreteness of wearing the appliance. In order to achieve good barrier properties, a typical barrier film will have a barrier layer of at least about 0.2 mils (5  $\mu\text{m}$ ) in thickness.

Suitable film structures include, for example, a symmetrical five-layer film with a core barrier layer, adjacent adhesive layers on either side of the barrier layer, and outermost skin layers on each side of the film. Such multi-layer structure can symbolically be represented as a "ABCBA" structure, wherein the "C" layer is a barrier layer, the "B" layers are adhesive tie or bonding layers, and the "A" layers are skin layers. A representative 4.0 mil (100  $\mu\text{m}$ ) film might have a "C" barrier layer of PVDC or EVOH or PETG at 10% of the overall gauge; "B" adhesive tie layers of EVA or EVA-g-MAH at 10% each of overall gauge; and outermost "A" skin layers of LLDPE, mPE or coPP at 35% each of the overall gauge. This can be represented as a 35/10/10/10/35 layer ratio of the 4.0 mil (100  $\mu\text{m}$ ) film. A possible 5-layer asymmetrical film structure can be represented as ABCBD, wherein the "D" layer is a different skin material than the "A" material. Another representative barrier film structure that is useful in making ostomy or collection bags is a 4-layer asymmetrical structure. This can be represented as "ABCB" wherein the "C" layer is a barrier layer, the "B" layers are adhesive tie or bonding layers, and the "A" layer is a skin layer. In this case, the exposed "B" adhesive layer can be used to thermally bond or seal two plies of the film together, such as during heat sealing of a bag seam.

For ostomy bags, urological collection bags and other appliances which are worn against the body, it is desired that they exhibit excellent haptics, softness and comfort. Use



- of woven and nonwoven laminates or coverings over the bag is commonly used to eliminate the direct contact of a plastic film against the skin. Direct contact of a smooth film can cause perspiration and "clinging" of the film to the skin, can cause blisters and sores to form due to abrasion against the skin in addition to hot and moist contact, and can promote
- 5 bacteria or infectious growth between the bag and skin of the patient. The barrier properties of the containment bag or pouch, which are required to eliminate odor permeation of the excreted human waste products through the pouch, also prevent moisture in the form of skin perspiration from escaping from the region where the pouch or appliance is worn. Use of a one or two fringed layers according to the present invention as
- 10 skin layer or layers 'A' provides the desired soft skin contact and can allow perspiration to escape from behind the appliance. It is further desired that films with low flexural or tensile modulus and low durometer "hardness" be used for the outermost layers of the film so as to provide a softer, more conformable surface. Elastomeric films, such as those made from TPU, CPE, styrenic block copolymers, ESI and homogeneous polyolefin resins, are
- 15 especially preferred for coextruded layers on an ostomy or collection bag. These films also promote quietness, which a desired attribute of a bag or pouch appliance. A patient wearing a pouch desires the appliance not to make any noise or rustling sound while moving around, as commonly occurs when conventional plastic films are flexed, folded or "crinkled".
- 20 It is additionally desired to utilize plastic tubing and/or plastic fittings or connectors on the film utilized for medical bags, pouches or appliances. These fittings and tubing are usually made of a material compatible with the film and bondable to the film. Tubing or fittings may be made of polyolefins such as polyethylene, EVA or EMA, or of TPU or flexible vinyl (PVC). Film structure and surface compositions may need to be formulated so as to
- 25 provide suitable bonding via thermal welding, impulse sealing, high frequency (also known as radio frequency) sealing or mechanical fastening. Additionally, use of liquid curable adhesives or hot melt applied adhesives can be utilized to adhere tubing or fittings to a bag structure.

- In yet another aspect, the present invention relates to a floor or wall covering
- 30 product comprising a fringed film, sheet or coating according to the invention. In a preferred embodiment, the floor or wall covering is a multi-layer film or sheet comprising at least one layer having a fringed surface microstructure. The product may further comprise an optional print layer, an optional reinforcement layer and/or an optional foam backing layer. In a wall covering product, the fringed layer may be present, for example, as the surface or top layer,

the print layer or both. (Why not also the back layer, to store the glue?) In a floor covering product, the fringed layer may be the surface layer, the print layer and/or the backing layer, the fringed microstructure facing the floor. Used as a surface layer, the fringed microstructure is designed to afford soft touch and feel and may be imprinted, if desired. If the fringed layer serves as a print layer, the fringed microstructure is designed to provide proper surface variability and imprintability. This layer is imprinted and preferably covered (on the top) by a transparent upper wear layer. As a backing layer the fringed layer affords anti-slip properties. If present, the reinforcement layer is an intermediate layer providing dimensional stability to the product, preferably a floor covering, which can be in excess of 4 meters in width. The optional intermediate reinforcement layer may be a melt processed polyolefin polymer or a non-woven or woven textile material. Preferably, the optionally intermediate reinforcement layer is a non-woven glass fleece material or a non-woven polymeric material. If present, the foam backing layer imparts resilient cushioning properties to the product and can also impart noise and thermal insulation characteristics to the product as well as provide a barrier against microorganisms. Suitable resilient foam backing layers comprise or consist of a solvent dispersed polyolefin polymer, a melt processed polyolefin polymer or a latex composition. The product may further contain appropriate additives, e.g. flame retardant additives to insure compliance with flame retardant requirements and other regulatory requirements.

20

### Examples

The following Examples are illustrative of the invention, but are not to be construed as limiting the scope thereof in any manner. The following abbreviations are used: ESI = substantially random ethylene/styrene interpolymers; MFI or MI = melt flow index (measured at 2.16 kg/190°C according to ASTM D-1238, condition E); N/T = not tested; the pressures are indicated in MegaPascal (MPa) and the temperatures are in degree Celsius.

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### Example 1: Three-layer coextruded precursor films

A calendar comprising two steel rolls is used to produce three-layer coextruded precursor films which are surface textured on one outer layer. The upper roll is electrically heated. The lower roll or matrix roll is coated with a crosslinked fluorelastomer, laser microperforated and provides means for temperature control. The coating layer contains 2500 microholes per square centimeter. The holes are round and 200 microns long. An external heating device (hot air fan) to preheat the film surface is available and used as

30

required. Variable parameters are: calender speed, roll temperature (film temperature), roll gap and roll pressure.

The three-layer coextruded film with an outer layer having a low Vicat softening point is pressed against the perforated roll to create a surface textured side with knobs of variable length (depending on the temperature of the perforating roll, film-temperature and the pressure). Subsequently, the surface textured sides of these 'precursor films' are brushed or scrubbed in an off-line process to obtain fiber-like deformation and create a fringed film.

The three layer coextruded (basic) films used to prepare the precursor films have the following general structure:

Outer layer/ Backing layer A/ Backing Layer B.

In each of these films: the outer layer is made from a blend of 73% ENGAGE™ 8401 and 27% ENGAGE™ 8402 resins, both available from DuPont Dow Elastomers; backing layer A serves to provide bulk and is made from LDPE resin, e.g. LDPE 300R available from The Dow Chemical Company; and backing layer B has a varying composition (and function), being made from:

- a) VLDPE or ULDPE resin, such as ATTANE™ SL 4101 available from The Dow Chemical Company
- b) HDPE
- c) Polypropylene
- d) Ethylene Acrylic Acid Copolymer.

Each of the three layers may optionally further contain pigments, mineral fillers, plasticizer and/or migratory additives.

The three layer structures are 60 microns, 80 microns and 100 microns thick. In each structure, the outer layer makes up 60 percent of the overall thickness and the backing layers each make up 20 percent.

#### Example 2: Three-layer fringed films

The outer layers of the precursor films of Example 1 are mechanically treated with the following devices:

- Rectangular, flat phosphor bronze brush, filaments having a diameter of  $\phi 0.2$  and a length of 25 mm.

- Rectangular, flat bronze brush, filaments having a diameter of 0.15 and a length of 20 mm.
- Round bronze brush, round, filaments having a diameter of 0.15 and a length of 20 mm.
- Round glass fiber brush, filaments having a diameter of 0.2 and a length of 20 mm.
- Round abrasive fabric (PET nonwoven impregnated)
- 5    - Rectangular, flat abrasive fabric (PET nonwoven impregnated),
- Sandpaper
- Steel wool.

- The flat brushes are used to brush the film, stretched over a polyethylene cylinder (diameter of 5 cm) with unidirectional and circular movements in various film orientation directions.
- The round brushes are fixed on a conventional drill running at different speeds.
- The abrasive fabric, sandpaper or steelwool is used in unidirectional and oscillating movements at various speeds. Best results with respect to regularity of the fringed surface and soft, velvety textile-like touch are obtained with oscillating or multidirectional
- 15    movements using an abrasive fabric. The created fringes are up to 250 to 280 microns long.

- If during formation of the precursor film the polymer is allowed to fully solidify on the matrix roll such that more than 90% of the polymer is cooled down well below the Vicat softening point of the polymer before the film is removed, a satisfactory fringed surface quality is achieved even without subsequent brushing or scrubbing.
- 20

Example 3: One-layer fringed film comprising substantially random ethylene/styrene interpolymers (ESI)

- The precursor film is made from a composition containing the following ingredients,
- 25    the numbers in brackets indicating weight percent:
- ESI-1 Blend(50.6)
- ESI-2 (36.8)
- Polystyrene STYRON™ 648 (4.6)
- Zinc Stearate  $ZnSt_2$  (0.46)
- 30    Irganox B225 (0.18)
- $CaCO_3$  (5.6)
- $TiO_2$  Kronos 2220 (1.67)
- Other additives (0.09).

- ESI-1 Blend is a blend of ESI-1 (MFI: 1 g/10 min; copolymer styrene content: 30%; atactic polystyrene: below 10 %) and HDPE IP 60 (MFI: 60 g/10 min, density: 0.952 g/cc) in
- 35

a ratio of 75:25. The blend has a calculated MFI of 22 g/10 min and a calculated styrene content of 22 %. ESI-2 has a MFI of 1.0 and a styrene content of 69 %.

The monolayer basic film having a thickness of 70 microns is formed into a precursor film using the equipment described in Example 1 above. To prevent sticking of the film to the (upper) steel roll, aluminum foil was placed between the ESI and the steel roll, the foil serving as sacrificial or protective backing layer which is subsequently removed from the precursor film. Brushing of the precursor film yields a fringed film having a soft, velvety and textile-like feel.

In general it is expected that all film or sheet substrates exhibiting a melting point of  $> 20^{\circ}\text{C}$  compared to the fringe layer material or providing good release properties to molten polymers can be used as sacrificial layers. It is also expected that the same performance be achieved when such materials are coextruded with the fringe layer material.

#### Example 4: Fringed film comprising poly(lactide)

A three-layer co-extruded A/B/A cast film of the composition 15/70/15 Bionolle 1001 + 17%  $\text{TiO}_2$ /EcoPLA 4002/Bionolle 1001 + 17%  $\text{TiO}_2$  is formed into a precursor film. EcoPLA 4002 is available from Cargill Dow and consists of poly(lactide) (12.5 % D isomer + 20% Citroflex A4 (acetyl tri-n-butyl citrate). Bionolle 1001 is an aliphatic polyester (polybutylene succinate) available from Showa High Polymer Co. Ltd.. Using the equipment and techniques described in Example 1, the basic film is formed into a precursor film which is subsequently brushed to give a fringed film having a soft, velvety touch.

#### Example 5: Water Repellency of Fringed Film

To examine the water repellency or water management characteristics of fringed film the water contact angle test is utilized. Testing is done according to ASTM D- 5946 utilizing method 1 in 3.1.2.1. In this test method water droplets are placed on the surface of a film sample, and the contact angle values are measured and then averaged. The contact angle is measured directly with a protractor by using tangential alignment of a cross-hair line to the point at which the side of the water droplet contacts the substrate. Water contact angle can then be related to wetting tension via a conversion chart. This test is used to compare the effect that the fringed surface microstructure has on the water repellency or the ability to enable the water to bead up on the surface.

- It is found that the fringed film gives approximately 40 to 45 percent higher contact angle measurements as compared to non-textured films indicating that the fringed surface allows more water to bead up than the control. Such effect is important for applications requiring water repellency, such as raincoats and other water repellant outerwear, house wraps, feminine hygiene and diaper top sheets, and (latex) gloves (prevent formation of a slippery surface).

#### Example 6: Physical Properties

- Tensile and tear properties are determined for a three-layer fringed film (layer ratios: 50% fringed/ 30% core/ 20% outside) of the following composition:

- fringed layer: 6 wt.% slip masterbatch, 27 wt.% of a homogeneous ethylene/octene copolymer having a density of 0.885 g/ccm and a MFI of 30 g/min, 67 wt.% of a homogeneous ethylene/octene copolymer having a density of 0.902 g/ccm and a MFI Of 30);
- core layer: 87 wt.% LDPE 300R, 13 wt. % White Masterbatch;
- outside layer: 92 wt.% HDPE 35060E (density: 0.960 g/ccm, MFI 0.29 g/10 min), 8 wt.% White Masterbatch.

- A smooth (non-textured) base film of the corresponding structure and composition is used as control. Machine and cross direction tensile peak loads are determined according to the ASTM D-882 method, Elmendorf tear testing is performed according to ASTM D-1922.

Sample	Test	Cross Direction	Machine Direction
Control	Average Peak Load	9.7 lb/f	9.8 lb/f
Fringed	"	8.9 lb/f	11.0 lb/f
Control	Average Tensile Yield Load	5.6 lb/f	5.2 lb/f
Fringed	"	6.4 lb/f	5.9 lb/f
Control	Elmendorf Tear	667.2 g	206.4 g
Fringed	"	899.2 g	190.4 g

#### Example 7: Fringed Film comprising polyvinyl chloride (PVC)

- A composition consisting of the following components and amounts is gelated on a roll mill and converted into a 100 micron film:

s-PVC, K 50	100 phr
DOP (dioctylphthalate)	30 phr
Ba-Zn stabilizer (metalcarboxilate)	3 phr
ESBO (epoxidized soybean oil)	0.5 phr

- 5 Using a compression molding process, solid fringes with a length of 120 microns are obtained.

WHAT IS CLAIMED IS:

1. A mono-layer or multi-layer film, sheet, or coating wherein at least one layer  
5 displays a surface microstructure, which layer comprises a thermoplastic polymeric material selected from the group consisting of
- a biodegradable polymer, preferably poly(lactide),
  - a polyvinyl chloride, and
  - a polyolefin interpolymer comprising
- 10 i) polymer units derived from at least one of ethylene and/or an alpha-olefin monomer; and
- ii) polymer units derived from one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, or a combination of at least one aromatic vinyl  
15 or vinylidene monomer, and
- iii) optionally polymer units derived from one or more ethylenically unsaturated polymerizable monomer(s) other than those derived from i) and ii),
- and which layer is characterized by substantially solid fibril-like fringes.
- 20 2. A mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer is a cured, irradiated or cross-linked thermoplastic polymeric material and which layer is characterized by substantially solid fibril-like fringes.
- 25 3. A mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes, and wherein at least one layer is a foamed layer.
- 30 4. A mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes, and wherein at least one layer is elastic,



5        5. A mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes, and wherein at least one layer has been oriented.

10       6. A mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes, and wherein at least one layer is printed or imprinted, preferably the layer having the fringed surface microstructure.

15       7. A mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes, wherein the surface microstructure has been subjected to a post treatment step selected from the group consisting of corona treatment, curing, irradiation and crosslinking.

20       8. A glove comprising a mono-layer or multi-layer film or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

25       9. A medicinal collection bag, preferably an ostomy bag, comprising a mono-layer or multi-layer film or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

30       10. A floor or wall covering product comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

11. An water repellant article of manufacture comprising a mono-layer or multi-layer film, sheet, or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

12. A packaging article comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

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13. An article of manufacture which has anti-skid properties, said article comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

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14. A heat resistant article of, said article comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

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15. A process for making a fringed film, sheet, or coating, said process comprising  
- providing a foamed precursor film, sheet, or coating with a surface characterized by a pattern of peaks and valleys, and  
subjecting said precursor to mechanical treatment under conditions allowing the

20 formation of a fringed surface microstructure.

16. Use of a film, sheet or coating comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes to make an article which is water repellant.

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17. Use of a film, sheet or coating comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes for packaging.

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18. Use of a film, sheet or coating comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a

thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes to make an article with enhanced carrying, capturing or storing properties.

19. Use of a film, sheet or coating comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes to make an article which has anti-skid properties.

20. Use of a film, sheet or coating comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes to make an article which has enhanced heat resistant.

21. Use of a film, sheet or coating comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes as a filtration medium or to make a filtering device.

22. Use of a biodegradable polymer, preferably poly(lactide), to make a film, sheet or coating comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material and is characterized by substantially solid fibril-like fringes.

23. Biodegradable article of manufacture comprising a mono-layer or multi-layer film, sheet or coating wherein at least one layer displays a surface microstructure, which layer is a thermoplastic polymeric material, preferably poly(lactide), and is characterized by substantially solid fibril-like fringes.

## INTERNATIONAL SEARCH REPORT

 Interna Application No  
 PCT/US 00/19319

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 B29C59/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 518 865 A (HOESSEL PETER ET AL) 21 May 1996 (1996-05-21) column 3, line 7 - line 11; example 1	1
X	EP 0 275 653 A (ICI PLC) 27 July 1988 (1988-07-27) column 3, line 9 - line 14 column 3, line 48 - line 52	1
X	GB 1 158 471 A (IMPERIAL CHEMICAL INDUSTRIES) 16 July 1969 (1969-07-16) example 1	1
X	DE 195 24 076 C (HCD HYGIENIC COMPOSITES DEV GM) 24 October 1996 (1996-10-24) cited in the application column 3, line 24 - line 27	1
-/-		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search

20 October 2000

Date of mailing of the international search report

03. 11. 00

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# INTERNATIONAL SEARCH REPORT

Internal Application No  
PCT/US 00/19319

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 208 773 A (ICI LTD) 28 June 1974 (1974-06-28) page 13, line 11 - line 16; figures	1
X	US 3 895 153 A (JOHNSTON MANLEY R ET AL) 15 July 1975 (1975-07-15) examples	1
P, X	DE 198 12 097 C (WAGNER) 2 September 1999 (1999-09-02) example 2	1

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 00/19319

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 2-23  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 2-23

In view of the large number and also the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and concise), namely claim 1.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/US 00/19319

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5518865 A	21-05-1996	DE 4141352 A AT 163096 T DE 59209181 D EP 0547419 A ES 2111601 T JP 5273758 A	17-06-1993 15-02-1998 12-03-1998 23-06-1993 16-03-1998 22-10-1993
EP 0275653 A	27-07-1988	AT 64845 T AU 605528 B AU 8257387 A CA 1298938 A DE 3771199 D DK 2188 A FI 875701 A JP 63181755 A NO 875260 A, B,	15-07-1991 17-01-1991 14-07-1988 21-04-1992 08-08-1991 08-07-1988 08-07-1988 26-07-1988 08-07-1988
GB 1158471 A	16-07-1969	NONE	
DE 19524076 C	24-10-1996	AT 196442 T AU 6418496 A WO 9702128 A EP 0836549 A JP 11508501 T	15-10-2000 05-02-1997 23-01-1997 22-04-1998 27-07-1999
FR 2208773 A	28-06-1974	GB 1451311 A AR 201674 A AT 364067 B AT 816977 A AT 344656 B AT 1014273 A AU 6284873 A BE 807879 A CA 1043068 A CA 1045322 A CA 1045323 A CH 566203 A DE 2359565 A DE 2365824 A DK 12888 A, B, DK 155190 B ES 421129 A IN 140101 A JP 49087762 A NL 7316259 A SE 393765 B SE 417291 B SE 7608985 A US 4451419 A US 4436687 A US 4436503 A ZA 7308898 A	29-09-1976 08-04-1975 25-09-1981 15-02-1981 10-08-1978 15-12-1977 29-05-1975 27-05-1974 28-11-1978 02-01-1979 02-01-1979 15-09-1975 27-06-1974 12-08-1976 12-01-1988 27-02-1989 16-04-1976 11-09-1976 22-08-1974 06-06-1974 23-05-1977 09-03-1981 11-08-1976 29-05-1984 13-03-1984 13-03-1984 25-06-1975
US 3895153 A	15-07-1975	AU 467758 B AU 7402274 A DE 2447989 A GB 1481876 A JP 869353 C	11-12-1975 11-12-1975 24-04-1975 03-08-1977 13-07-1977



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19319

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3895153 A		JP 50065536 A JP 51044010 B	03-06-1975 26-11-1976
DE 19812097 C	02-09-1999	AU 3413899 A WO 9947339 A	11-10-1999 23-09-1999